Fractal Considerations in Chromatography: Column Efficiency and the Multimicrocolumn System

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The first part of this paper uses only fractal geometry mathematics to study the variations in column efficiency (h) with its geometrical characteristics (both column and particle diameter,...) and constant column length. In this case the fractal dimension D of h was 2. Conventional results in chromatography were found with this theory independent of the others. For example, a decrease in the particle diameter filling the column must theoretically increase column efficiency. In a second part, geometry was linked to hydrodynamic considerations to study the effect of the microcolumn structure and its organization in a multimicrocolumn chromatographic system. It demonstrated that to minimize the pressure drop, the geometric structure must obey a power law. This system uses columns with a low diameter and a low pressure drop to perform efficient separation.

Introduction

Fractal geometry has provided a mathematical formalism for describing complex and dynamical structures.[1] It has been applied successfully in a variety of areas such as astronomy,[2] economics,[3,4] or biology.[5,6] Because of its success in this variety of areas, it is natural to develop fractal applications in chromatography. The fractal concept was used to study the effect of surface irregularity on the accessibility to silylating reactions.[7] Grafting of surfaces is indeed a key process in the preparation of chromatographic materials,[8−11] given the ability to fine-tune the type of surface absorbate interactions by a suitable choice of the derivatizing agent.[12] In recent years, to study the surface properties of chromatographic materials in general and reversed-phase materials in particular, photophysical probes have been successfully used. The structure of the derivatizing layer has been an issue of much debate regarding the questions of whether silanols are evenly distributed on the surface of silica[13] or whether they are heterogeneously clustered.[14] Lochmuller et al. have used the intermolecular complexation process between ground-state and exited-state pyrene to investigate this problem.[15,16] The effect of surface irregularity on parameters such as surface concentration was studied by Farin and Avnir.[17] Another application in chromatography was proposed to study the solute retention on immobilized human serum albumin (HSA). This study proposes a mathematical model to provide a more realistic understanding of the molecular processes that take place in the sucrose dependence of dansylamino acid binding on the HSA site II cavity.[18] In a first section, using only fractal considerations, the variation in efficiency in relation to geometrical characteristics was studied. It is rare for a novel theory, independent of others and addressing a basic problem, to yield results that are virtually identical. This is the case reported here. The aim of the second section was to make an analysis of a multimicrocolumn systems (MCS) in terms of not only its geometry but also in terms of hydrodynamics.

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Demonstration of Fractal Nature of Column Efficiency. A novel theory using the fractal concept was proposed to study the effect of the variation of some current geometrical characteristics of a chromatographic column on its efficiency. Usually for the same solute, the plate height that characterized the column efficiency depends on some geometrical characteristics of the column, that is, (a) its length L and its diameter d_1, (b) the column packing, which is usually treated as a three-dimensional network of pores with an average diameter d_2 that is linked to the average particle diameter d_3 by the equation[19]

$$d_2 = 0.42 d_3 \frac{n}{n-1} \quad (1)$$

where n is the interparticle porosity, and (c) some other geometrical characteristics d_i and the other “extra column” physical parameters (nature of the mobile phase, its flow rate...) remaining constant as set out below. In the plate theory, h was usually considered to have a length dimension. h is some complicated functions of the various length scales L, d_1, d_2, d_3, ...d_i that paramatrize the size and shape:

$$h = h(L,d_1,d_2,d_3,...,d_i...) \quad (2)$$

On purely dimensional grounds this can be expressed as:

$$h(L,d_1,d_2,...,d_i...) = d_1\ \Xi\left(\frac{L}{d_1},\frac{d_2}{d_1},...,\frac{d_i}{d_1},...\right) \quad (3)$$

where Ξ is a dimensionless function of the dimensionless ratio L/d_1, and so on. Consider now a modification of the geometrical characteristic of the column by making a uniform scale transformation on all lengths d_i:

$$d_i \rightarrow d'_i = \delta d_i\ (i = 1, 2, 3, ...) \quad (4)$$

where δ is some positive arbitrary number L remaining constant. By this transformation h responds in the following manner:

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$$h \rightarrow h' = h(L,\delta d_1,\delta d_2,...,\delta d_i,...) = \delta d_1\, \Xi \left(\frac{L}{\delta d_1},\frac{d_2}{d_1},...,\frac{d_i}{d_1},...\right) \tag{5}$$

As L is fixed, the right-hand side is no longer simply proportional to δ. Although the δ dependence of Ξ was unknown, it can be parametrized as a power law reflecting the hierarchical fractal-like organization:

$$\Xi\left(\frac{L}{\delta d_1},\frac{d_2}{d_1},...,\frac{d_i}{d_1},...\right) = \delta^{\xi}\, \Xi \left(\frac{L}{d_1},\frac{d_2}{d_1},...,\frac{d_i}{d_1},...\right) \tag{6}$$

where ξ is an "arbitrary" exponent thus:

$$h \rightarrow h' = h(L,\delta d_1,\delta d_2,...,\delta d_i,...) = \delta^{\xi+1} h(L,d_1,d_2,...,d_i,...) \tag{7}$$

It is very important to note here that because L is fixed, h does not scale simply as δ. The exponent $D = \xi + 1$ can be interpreted as the fractal dimension of h.[1,20] As such, it satisfies $0 \leq \xi \leq 1$. The lower limit, $\xi = 0$, is the conventional Euclidian case; the upper limit $\xi = 1$ represents the "maximum fractality" of a surface-filling structure in which the length h scales like a conventional surface. It is well known that h is calculated by

$$h = h(L,\sigma) = \frac{\sigma^2}{L} \tag{8}$$

where σ^2 is the peak dispersion. σ has a length dimension and is dependent on d_i values σ (d_1, d_2, ...,d_i,....). During a δ scale transformation

$$h \rightarrow h'(L,\delta\sigma) = \delta^2 h(L,\sigma) \tag{9}$$

Combining eqs 7 and 9 gives $D = 2$ and $\xi = 1$. In conclusion, the fractal dimension of h is maximal (=2) rather than the canonical Euclidian value of 1. This result implies that (a) all the distances associated with the network are themselves fractal; (b) to decrease h, that is, to increase column efficiency, δ must be less than 1. This result is consistent with the well-known fact that to increase column efficiency the column and particle diameter must be decreased; (c) for a given δ the maximal fractal dimension of h gives the minimal value of h, that is, the best efficiency.

So far the model was structured around the geometry of hierarchical networks. In the second section, the proposed model was not only based on the geometry of a fractal network of branching microcolumns but also on hydrodynamic considerations.

Fractal Chromatographic System

Most authors[21,22] seem to be adhering to the general convention that restricts the term "microcolumn" to open tubular or packed capillary columns with internal diameters less than 0.5 mm, whereas "microbore" refers to columns with an internal diameter between 0.5 and 2.0 mm. For a steady laminar flow F, the viscous resistance z of a microcolumn with a uniform structure (length L and circular cross-section a) filled with particles is given by the well-known Darcy law:

$$z = \frac{L\eta}{\pi a^2 K^o} \tag{10}$$

where η is the viscosity of the mobile phase and K^o the microcolumn permeability constant that depends on the particle diameter filling it.

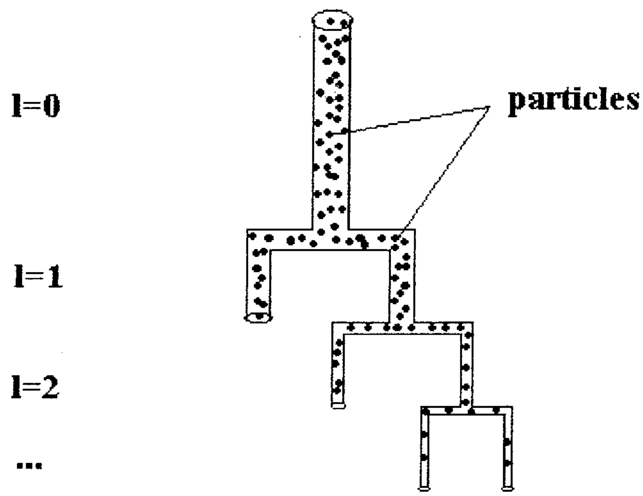

Figure 1. Representation of the fractal multimicrocolumn system (FCS). Here l is the order of the level, beginning with the microcolumns with the largest cross-section ($l = 0$) and ending with those with the smallest cross-section ($l = \omega$).

The corresponding pressure drop Δp is:

$$\Delta p = Fz \tag{11}$$

where F is the flow rate in the column.

Combining eqs 10 and 11 gives:

$$\Delta p = \frac{L\eta F}{\pi a^2 K^o} \tag{12}$$

The corresponding dissipation energy was

$$E = F\Delta p \tag{13}$$

and yields

$$E = \frac{L\eta F^2}{\pi a^2 K^o} \tag{14}$$

Minimizing the dissipated energy obviously leads to a decrease in the flow rate and column length or an increase in the circular cross-section radius. Consider now the case of a MCS. This system is composed of branching from the column with the highest cross-section (level o) to the lowest cross-section (level ω) (Figure 1). Each microcolumn ramifies into p_l smaller ones. At level l the microcolumn has a circular cross-section of radius a_l. The microcolumn length is L_l. The parameters

$$\alpha_l = \frac{a_{l+1}}{a_l} \tag{15}$$

and

$$\beta_l = \frac{L_{l+1}}{L_l} \tag{16}$$

characterize the ramifications of the MCS. Consider now the case of a uniform geometric structure, that is, $\alpha_l = 1$ and $\beta_l = 1$. If N is the total number of microcolumns with a z resistance, the resistance Z of the MCS is

$$Z = \frac{z}{n} \tag{17}$$

and using eqs 10, 11, 13, and 17 yields

$$E = \frac{L\eta F^2}{\pi a^2 n K^o} \quad (18)$$

This last equation shows that to minimize the dissipated energy E, n should not be too high. In the case of a MCS with self-similar fractal nature (FCS system), this implies that α_l, β_l, and p_l must be independent of l: $\alpha_l = \alpha =$ constant, $\beta_l = \beta =$ constant, and $p_l = p =$ constant. Thus at level l, the total number of microcolumns can be expressed as:

$$N_l = p^l \quad (19)$$

The volume of an empty microcolumn at level l is:

$$V_l = \pi {a_l}^2 L_l \quad (20)$$

Thus, the total volume V_t of an empty FCS system is

$$V_t = \sum_{l=0}^{\omega} V_l N_l \quad (21)$$

Combining eqs 19, 20, and 21 gives

$$V_t = \sum_{l=0}^{\omega} \pi a_l^2 L_l p^l \quad (22)$$

which yields

$$V_t = V_\omega p^\omega \frac{(p\alpha^2\beta)^{-(\omega+1)} - 1}{(p\alpha^2\beta)^{-1} - 1} \quad (23)$$

where V_ω denoted the volume in the smallest capillaries. This latter equation reflects the fractal nature of the system. For a steady laminar flow, the viscous resistance Z_l using eq 10 is:

$$Z_l = \frac{L_l \eta}{\pi {a_l}^2 K^o} \quad (24)$$

It was assumed that the small turbulence and nonlinearities at junctions of the microcolumns would be negligible. Therefore, the resistance Z of the FCS (Z_{FCS}) is:

$$Z_{FCS} = \sum_{l=0}^{\omega} \frac{Z_l}{N_l} \quad (26)$$

Combining eqs 19, 24, and 26 gives

$$Z_{FCS} = \sum_{l=0}^{\omega} \frac{L_l \eta}{\pi {a_l}^2 K^o p^l} \quad (27)$$

and yields:

$$Z_{FCS} = \frac{Z_\omega}{p^\omega} \frac{\left(\frac{p\alpha^2}{\beta}\right)^{(\omega+1)} - 1}{\left(\frac{p\alpha^2}{\beta}\right) - 1} \quad (28)$$

where Z_ω denotes the resistance in level ω.

As the mobile phase is maintained as it flows through the FCS,

$$F_o = N_l F_l = N_\omega F_\omega \quad (29)$$

and

$$\Delta p = F_o Z_{FCS} \quad (30)$$

where F_l and F_ω are the flow rates at level l and in the smallest microcolumn (level ω) and Δp the corresponding pressure drop.

By using eqs 13, 28, and 30 the corresponding dissipation energy was

$$E = \frac{{F_o}^2 Z_\omega}{p^\omega} \frac{\left(\frac{p\alpha^2}{\beta}\right)^{(\omega+1)} - 1}{\left(\frac{p\alpha^2}{\beta}\right) - 1} \quad (31)$$

Equation 31 leads to the important conclusion that E depends on the geometrical characteristics of the FCS, that is, on a_l, L_l, and p: $E(a_l, L_l, p)$. Minimizing the dissipated energy inside the FCS using the standard method of Lagrange multipliers leads to the equation:

$$\alpha_l = p^{-1/2} \quad (32)$$

This equation is independent of the microcolumn cross-section. This equation predicts that energy-carrying waves are not reflected back up the microcolumns at branch points and that the branching is area preserving. Assuming that the sum of the cross-sectional areas of the daughter branches equals those of the parent (Figure 1), then

$$\pi {a_l}^2 = p\pi a^2_{l+1} \quad (33)$$

yields

$$\frac{a_{l+1}}{a_l} = p^{-1/2} = \alpha_l \quad (34)$$

To minimize the dissipated energy in the FCS, the area must be maintained to respect the largest microcolumn. In conclusion, in the first part, by using fractal geometry defined by Mandelbrot, the fractal nature of the height to a theoretical plate (h) was demonstrated. The determination of its fractal dimension demonstrated that for a given column length, h scales like a conventional surface. Therefore, minimizing h is obtained by minimizing some geometrical characteristics of the column such as column and particle diameter. This novel theory, which is completely independent of the others, provided confirmation of these classical results. In the second part, a theoretical study combining energetics with fractal design demonstrated the need to organize the microcolumns into a multimicrocolumn chromatographic system. It was shown that a fractal distribution of the microcolumns associated with the power law minimizes the dissipated energy and, thus, the corresponding pressure drop. Practically, the pressure drop is the inevitable result of filled column with a very low diameter. The FCS can use microcolumns with a small pressure drop to perform efficient separation. To the best of our knowledge, there are no measurements of these effects under the conditions specified here to confirm the predicted trends, but it is anticipated that systematic experimental studies aimed at addressing these issues will appear soon. Therefore, this model could be a useful starting point for a more refined analysis of multimicrocolumn chromatographic phenomena.

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