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## Modeling of radial heterogeneity in chromatographic columns II. Separation of a two-component mixture on a column with cylindrical symmetry

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### Abstract

The elution band profiles of two partially separated components were calculated for a radially heterogeneous cylindrical column, using a modified equilibrium-dispersive model, assuming no radial dispersion. Steady-state flow-rate is assumed with a given cylindrical radial distribution of the velocity. The results show a marked degradation of the column performance when the ratio of the mobile-phase velocities at the column center and at the wall differs from unity by more than a few percent.

*Keywords:* Elution band profiles; Band profiles; Cylindrical symmetry; Columns, radially heterogeneous cylindrical

### 1. Introduction

The theory of chromatography has almost always assumed that the column is radially homogeneous and that the radial distribution of the mobile-phase flow velocity is flat, i.e., is well described by the plug flow condition [1]. Experimental results have falsified this assumption every time systematic determinations of the radial distribution of the mobile-phase velocity across a chromatographic column have been carried out [2–7]. Nevertheless, attention has only recently been focussed on the consequences in non-linear and preparative chromatography of a non-plug distribution [7]. The recent work by Yun

and Guiochon [7] was devoted to the extension of the ideal model solution to the case of a radial distribution of the mobile-phase velocity in an ideal column, i.e., a column in which mass transfer between phases is instantaneous and there is no axial dispersion. The third condition of the ideal model [1], plug flow, was relaxed. The work was limited to the single-component case and six types of flow distributions were considered, parabolic with extremum velocity at the column center, parabolic with extremum velocity at the center, and sinusoidal, with an extremum at the column center [7]. Important and characteristic changes of the elution band profiles were shown to take place as soon as the ratio of the maximum and the minimum velocities exceeded unity by more than a few percent. Although a concentration shock propagates along each parallel to the column axis, all the band profile recorded by a bulk detector appears to harbor a front shock layer.

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The band top is somewhat eroded in the cases which are most similar with actual experimental profiles.

The marked differences observed between experimental profiles and these theoretical results largely exceed those which could be expected for an ideal model solution [1]. They suggest that either the flow pattern in actual columns does not deviate much from plug flow or the model does not take into account an important feature of flow in actual columns. The first possibility does not seem to agree with independent results regarding the compressibility of the packed beds in large-size chromatographic columns [8,9]. Among the reasons why the ideal model could be unrealistic, we can list the following: (i) radial dispersion in packed columns could contribute significantly to relax the influence of a radial velocity distribution (this is quite doubtful in view of independent results regarding radial or transverse dispersion [3,4,10]); (ii) the streamlines are not parallel to the column axis (if the fastest streamlines are somehow longer than average, this could compensate for the apparent spreading due to a cylindrical distribution of the flow velocity); and (iii) the velocity distribution is closed to plug flow in a large part of the cross-section area of the column.

Be like as it may, the importance of radial column homogeneity, which still appears to be minor in modern analytical high-performance liquid chromatography (HPLC), is quite an important problem in preparative scale applications. The much larger size of the column enhances the possibility of large-scale fluctuations of the packing density, hence of the local velocity of the mobile phase which could cause excessive losses in the column performance. As there are many reasons for which poor column efficiency and abnormal band profiles can be observed, it is useful to know which results each one of them can produce for diagnostic purposes. It would be easy to solve the problem of the separation of two components within the framework of the ideal model, assuming a given radial velocity profile, by following the same approach as for the single-component problem. This does not seem useful at this stage because of the complex features of the analytical solution of the two-component problem in the ideal model. It seems more useful to calculate and study solutions of the equilibrium-dispersive model of chromatography.

The goal of the present work is the discussion of such solutions and the investigation of the influence of various velocity distributions across the column. The calculation of the individual band profiles of the components of a binary mixture will allow the determination of the relationship between the amplitude of the variation of the velocity and the loss of recovery yield and production rate. This work should contribute to improve our understanding of the process of preparative chromatography.

## 2. Theory

The equilibrium-dispersive model of chromatography is a modification of the ideal or equilibrium model which consists in keeping the dispersive term in the differential mass balance and further replacing the axial dispersion coefficient by a larger, apparent dispersion coefficient to account for the resistance to mass transfer between the two phases in the column [1]. The equilibrium between these phases is assumed to be achieved instantaneously, however. This model has been used extensively and successively in the calculation of band profiles for single-component and multicomponent mixtures in classical non-linear chromatography, assuming that the column can be considered as unidimensional. It has been shown that its solutions agree well with experimental results whenever the kinetics of mass transfer between and across the phases of the chromatographic system are fast and the column efficiency exceeds a few hundred plates [1].

The new model used here is a variant of the equilibrium-dispersive model which considers a radial velocity distribution. It assumes constant local equilibrium between the two phases and accounts for the finite column efficiency by using an apparent axial dispersion coefficient which is the same as for an homogeneous, unidimensional column. In principle, such a model should also include a radial dispersion coefficient to account for the radial dispersive flux which takes place when radial concentration gradients arise. We know, however, that the radial [3,4] or transverse [10] dispersion coefficient is much smaller than the axial dispersion coefficient. Around the mobile phase for which the column efficiency is maximum, the radial dispersion coeffi-

cient is three times smaller than the axial dispersion coefficient. In the range of velocities typically used in chromatography, this ratio exceeds often one order of magnitude. Accordingly, the influence of radial dispersion can be neglected as a first approximation. That the contribution of radial dispersion is indeed often negligible has been shown recently in a study of the migration and broadening of a cylindrical pulse, coaxial with the column but of narrower diameter [11]. In most practical cases, the pulse will not broaden in the radial direction to the point that its concentration becomes significant at the wall before its elution. Accordingly, an extension of the equilibrium-dispersive model which neglects radial dispersion could be a realistic, practical solution for the elution profile of the components of a binary mixture at the exit of a cylindrical column.

### 2.1. Mathematical model of the system.

The differential mass balance equations of the two components are written

$$\frac{\partial C_1}{\partial t} + F \frac{\partial q_1}{\partial t} + u(r) \frac{\partial C_1}{\partial z} = D_a \frac{\partial^2 C_1}{\partial t^2}$$

$$\frac{\partial C_2}{\partial t} + F \frac{\partial q_2}{\partial t} + u(r) \frac{\partial C_2}{\partial z} = D_a \frac{\partial^2 C_2}{\partial t^2}$$

where  $C_i$  and  $q_i$  are the mobile and stationary phase concentrations of component  $i$  ( $i = 1$  or  $2$ ), respectively;  $u(r)$  is the linear velocity of the liquid phase;  $F$  is the phase ratio of the packing ( $F = (1 - \epsilon)/\epsilon$ , with  $\epsilon$  total column porosity); and  $D_a$  is the apparent axial dispersion coefficient, related to the column HETP. For the lack of more information, we assume that  $\epsilon$ , hence  $F$ , is constant in the entire column.

Since we assume constant equilibrium between the two phases,  $q_i$  and  $C_i$  are related by the equilibrium isotherm. In this work, we will assume that this isotherm is accounted for by the Langmuir equation. For component  $i$ , we have

$$q_i = \frac{a_i C_i}{1 + b_1 C_1 + b_2 C_2}$$

The initial condition of the problem is

$$C(z, r, t = 0) = 0$$

The boundary condition corresponds to the injection of a rectangular concentration pulse of width  $t_p$  and height  $C_0$ . We assume that the amount of feed injected is spread homogeneously over the entire inlet cross-section of the column (i.e., the radial injection profile is flat). We have previously discussed the relationship between the problems of a flat injection in a radially heterogeneous cylindrical column and of a radial distribution of the injection profile in a column with piston flow and we have shown that they are equivalent [7]. The boundary condition is written

$$C(z = 0, r, t) = C_0 \text{ for } 0 < t \leq t_p$$

$$C(z = 0, r, t) = 0 \text{ for } t_p < t$$

### 2.2. Calculation of numerical solutions

The procedure used is similar to the one employed in the calculation of elution band profiles in a radially heterogeneous cylindrical column in the framework of the ideal model [7]. The column is divided into  $n$  concentric annular columns of radius  $r$  ( $0 < r < R_c$ , with  $R_c$  the column radius) and thickness  $\Delta r = R_c/n$ . For the numerical calculations, we took  $n = 50$ . The velocity is assumed to be constant in each annular column. The elution profile at the end of each annular column is calculated as a solution of the equilibrium-dispersive model of chromatography. The elution profile at the end of the column is obtained by summing up the differential amounts eluted from all the annular columns at any given time and reporting this amount to the corresponding volume of mobile phase:

$$C_{\text{avg}}(t) = \frac{\sum_{i=1}^n 2\pi r_i \Delta r u(r_i) C(r_i, t)}{\sum_{i=1}^n 2\pi r_i \Delta r u(r_i)}$$

$$= \frac{\sum_{i=1}^n r_i \Delta r u(r_i) C(r_i, t)}{\sum_{i=1}^n r_i \Delta r u(r_i)}$$

where  $C_{\text{avg}}(t)$  is the cross-section average concentration,  $r_i$  is the radius of the  $i$ th annular column,  $u(r_i)$  is the mobile phase velocity in the  $i$ th column,

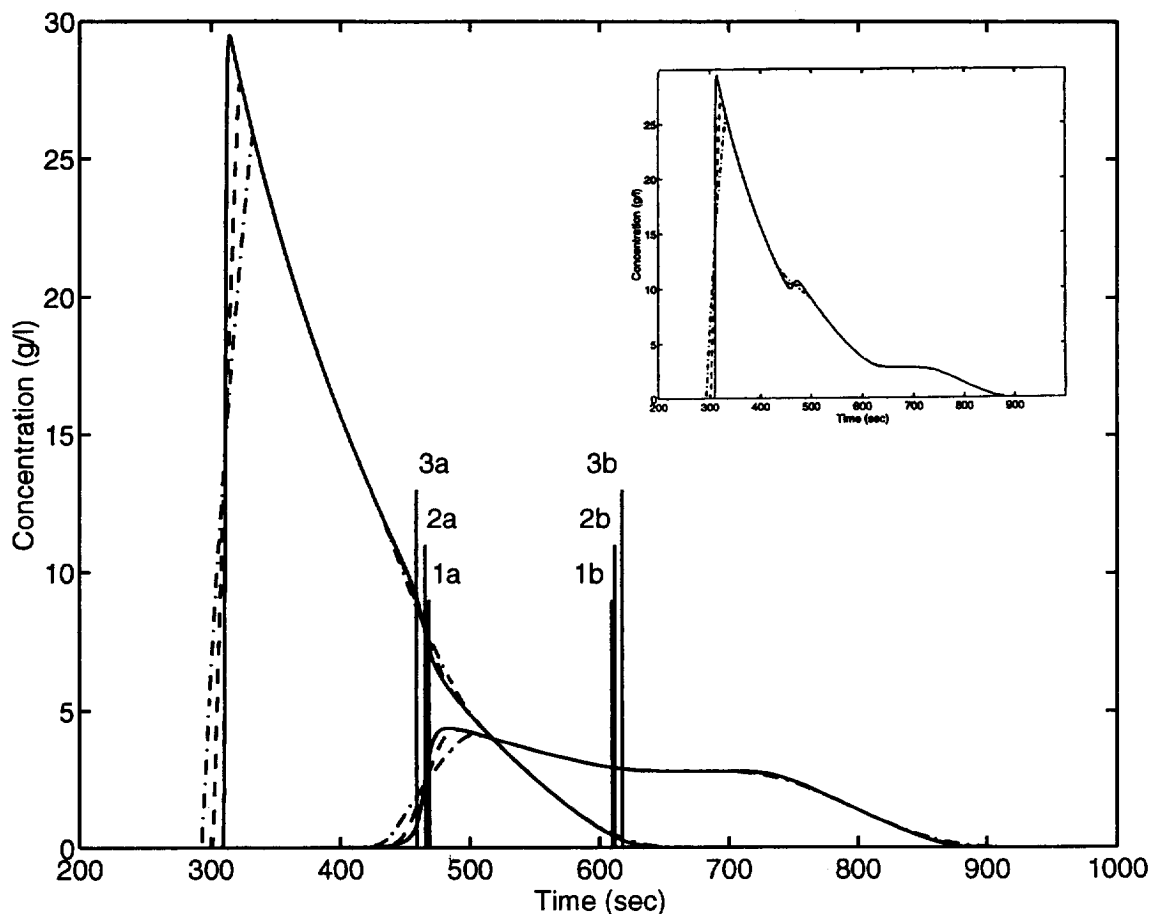


Fig. 1. Individual band profiles for a 3:1 mixture. Total loading factor, 20%. Column length, 15.0 cm; phase ratio,  $F = 0.4$ ; column efficiency, 3000 theoretical plates; Langmuir isotherm coefficients,  $a_1 = 12.0$ ,  $b_1 = 0.024$ ,  $a_2 = 16.8$ ,  $b_2 = 0.0336$ ; separation factor,  $\alpha = 1.4$ . Parabolic velocity distribution with maximum velocity at the column center; ratio of maximum to minimum velocity, solid line, 1.0 (piston flow); dashed line, 1.05; dash-dotted line, 1.10. Inset: total concentration profiles.

and  $C(r_i, t)$  is the elution band profile given by the equilibrium-dispersive model for the  $i$ th annular column.

The chromatograms obtained are presented as plots of the concentrations of the two components versus time. There are no convenient normalization parameters allowing a simplification of these profiles. Also given on the figures are the cutting points for the production of 99% pure fractions.

### 3. Results and discussion

Typical results of the calculations are shown in Figs. 1–3. The main figures correspond to the

individual band profiles of the two components, with relative compositions of the binary mixtures of 3/1 (Fig. 1), 1/1 (Fig. 2) and 1/3 (Fig. 3), respectively, with a total loading factor of 20% and a separation factor of 1.40. The insets show the corresponding total concentration profiles, as recorded by a non-selective detector. In all cases, the velocity profile is parabolic, with a maximum velocity at the column center. Note that these velocity profiles should not be mistaken for the Hagen–Poiseuille velocity profiles in empty tubes. As explained previously [7], there is a profound difference between the radial distribution of the velocities in an empty tube (Hagen–Poiseuille profiles, due to viscous friction along the wall) and in a packed column, in which the velocity dis-

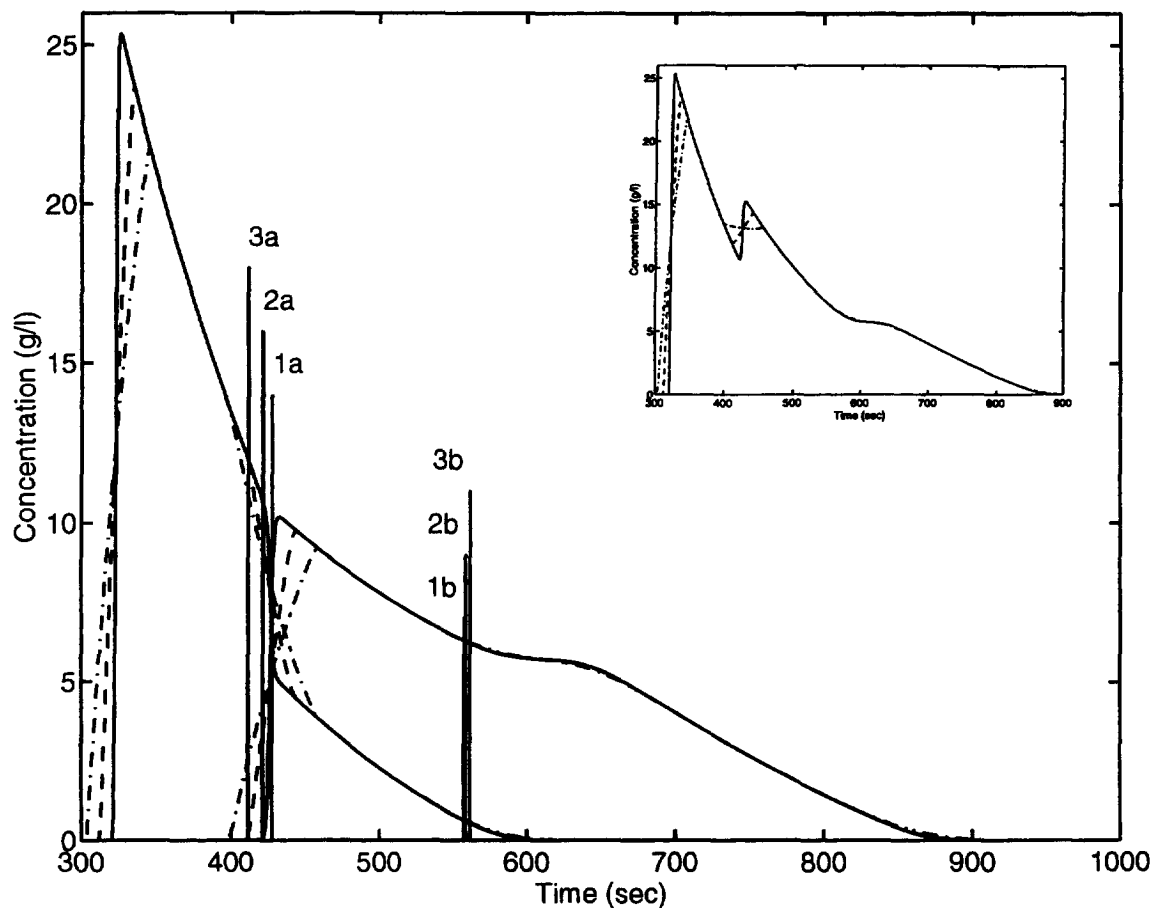


Fig. 2. Same as Fig. 1, but 1:1 mixture.

tribution is a consequence of a non-homogeneous packing density. Furthermore, the velocity in an empty tube is 0 at the column wall. In the present case, the velocities at the column wall and in its center are very close and the ratio of the extreme values of the velocity is close to unity. The parabolic profile was chosen because it is simple, yet close enough to the experimental results reported by Baur et al. [5] and by Farkas et al. [6] in analytical columns.

Three profiles are shown in each figure, corresponding to a ratio of the maximum velocity (center) to the minimum velocity (at the wall) of 1.00 (flat velocity profile or plug flow, presented for the sake of reference), 1.05 and 1.10. The main differences between the profiles obtained for various values of the highest to lowest velocity ratio is mainly around the shock layers of the two profiles. The effect of a

non-homogeneous velocity distribution is similar to that of a higher value of the coefficient of apparent axial dispersion, i.e., of a higher resistance to mass transfer. The front of the first component is less steep at high ratios and the shock layer between the two components is also much thicker. By contrast, the rear profile of the second component is nearly unchanged, although the column efficiency is relatively high (3000 theoretical plates). This profile is a diffuse boundary and is little affected by an apparent increase of the axial dispersion.

The vertical lines in the Figs. 1–3 correspond to the cutpoints for the preparation of 99% pure fractions. The first cutpoint (labelled 1a, 2a, or 3a) corresponds to the end of the collection of the purified first component. The second cutpoint (labelled 1b, 2b, or 3b) indicates the beginning of the collection of the second component of the mixture.

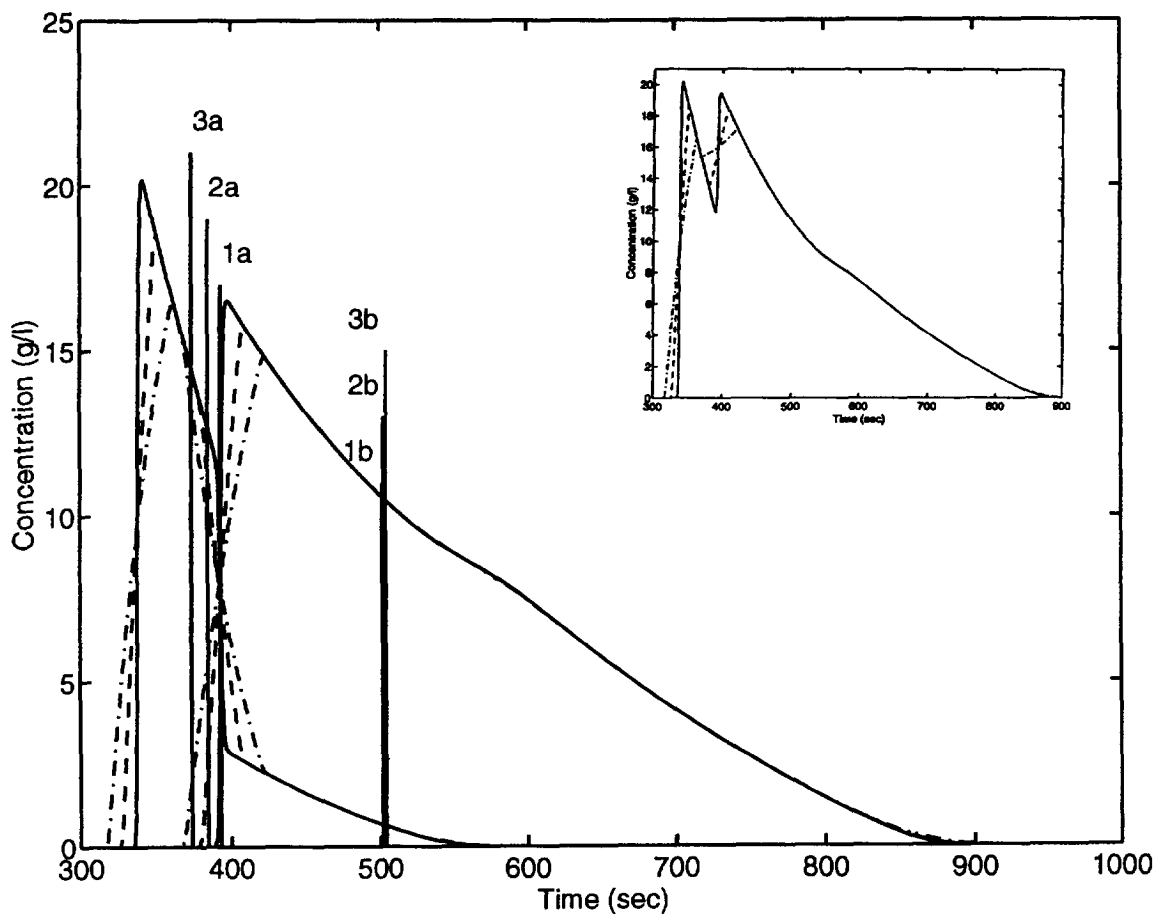


Fig. 3. Same as Fig. 1, but 1:3 mixture.

Table 1  
Cutpoints position (s)

Velocity ratio	99% A	98% A	99% B	98% B
<i>For a 1:3 mixture</i>				
1.00	392.98	393.72	501.49	474.36
1.05	384.49	386.73	502.43	474.83
1.10	373.80	376.47	504.08	476.01
<i>For a 1:1 mixture</i>				
1.0	427.42	429.31	557.47	541.59
1.05	421.29	425.45	558.73	542.30
1.10	411.38	417.20	561.87	544.58
<i>For a 3:1 mixture</i>				
1.00	468.78	476.25	609.84	599.33
1.05	465.63	475.54	611.88	600.80
1.10	458.56	471.37	617.39	605.04

Table 2  
Recovery yield (%)

Velocity ratio	99% A	98% A	99% B	98% B
<i>For a 1:3 mixture</i>				
1.00	81.47	81.89	55.61	65.10
1.05	71.64	73.87	55.36	64.99
1.10	57.30	60.54	54.94	64.67
<i>For a 1:1 mixture</i>				
1.0	84.23	84.79	50.97	55.81
1.05	81.09	82.80	50.70	55.63
1.10	75.52	78.29	49.89	55.07
<i>For a 3:1 mixture</i>				
1.00	86.95	88.51	49.94	52.82
1.05	86.00	88.23	49.44	52.50
1.10	83.75	86.92	48.04	51.45

The cutpoints 1, 2, and 3 correspond to the chromatograms obtained for different velocity profiles, 1 to the flat profile, 2 and 3 to the values of the ratio of the velocities in the center and at the wall of 1.05 and 1.10, respectively. The positions of the cutpoints are reported in Table 1 for two values of the fraction purity, 98 and 99%. The values of the recovery yield for the two components are given in Table 2. There is very little loss of recovery for the second compound, at most one percentage point. By contrast, the recovery yield of the first component decreases by nearly 30% for the 1:3 mixtures, in which case the displacement effect is strongest, which illustrates the consequences of the increased dispersion around the intermediate shock layer. The effect is lesser in the case of the other two mixtures because the displacement effect in the case of piston flow was less intense to begin with.

In conclusion, a modest degree of non-homogeneity of the column packing may have a relatively important adverse effect on the production rate and recovery yield observed in preparative chromatography.

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