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## Introduction

# On non-linear waves in chromatography

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The theory of multicomponent, non-linear, ideal chromatography is essentially based on the solution of systems of partial differential equations stating the differential mass balance of the components involved. The equations of a system are coupled by the competitive isotherms of the components involved. Glueckauf [1,2] was the first to give an analytical solution for two components with competitive Langmuir isotherms, both in the elution and the displacement modes. A comprehensive theory was later published by Rhee et al. [3–6], incorporating the progress made in the late 1940s by the mathematics of quasilinear partial differential equations [7,8]. They gave a straightforward, rigorous analytical solution of the problem. Considerable success has been encountered in this field recently, as a consequence of the easy availability of powerful computers. Helfferich [9] and Helfferich and Klein [10] had presented earlier a theoretical analysis of multicomponent, nonlinear, ideal ion-exchange chromatography based on the use of the *h*-transform and on definitions. Their different approach lead to essentially the same results [11].

Central to both mathematical solutions are the distance–time diagram, the method of characteristics, and the hodograph transform which play a major role in the calculation of the solutions (see below). While

the exact solutions are usually obtained most conveniently by referring directly to the relevant equations, these concepts provide the basis for the rapid determination of graphic solutions which are simple, clear, illustrative and didactic as lucidly explained in the following paper [12].

Although the theory of multicomponent, non-linear, ideal chromatography is complete for 25 years, its results still are not popular among chromatographers. Chemical engineers have applied it primarily for the calculation of band profiles in frontal analysis and displacement chromatography under isotachic conditions. The solutions are simple in these cases. Application to the more complex cases encountered in preparative liquid chromatography are almost as easy. Numerous studies have demonstrated that these solutions, although they neglect the influence on the band profiles of axial dispersion and the mass transfer kinetics, are close to experimental results [13], predict accurately the main features of the solutions [14–17] and can even serve as a guide for optimization purposes [18–21]. It is important for the chromatographer involved in the development of separation processes based on preparative chromatography to be able to derive easily an ideal model solution of the problem.

The main reason for the lack of popularity of the solution of the ideal model is the relative complexity of the mathematics of wave theory. This is especially

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so when two waves meet and interfere, that is when two component bands separate along a diffuse boundary. In such a case, an approximate solution is rather easy to derive from a geometrical construction. The following paper [12] presents the concepts and methods related to wave interference and coherence that permit an accurate quantitative construction of the column response to a variety of inputs. This material could be found so far only in the specialized literature and is buried in complex, theoretical papers. They were not easily accessible and are generally unknown among chromatographers. The authors have made great efforts to present them clearly and to illustrate their importance through reference to experimental results. They explain the coherence principle on which the theory is based, the phenomenon of band interference, and the progressive construction of composition paths in the composition space, distance-time diagrams and band profiles. The same method allows the determination of breakthrough fronts, elution band profiles and zone profiles in displacement chromatography, either before the isotachic conditions are reached or later, in the isotachic train. Although many chromatographers might find it difficult to follow the authors in all their developments, the effort will be rewarding as they should find here some useful tools to better understand the behavior of columns under non-linear conditions.

The method of characteristics<sup>1</sup> considers the propagation of concentrations as the propagation of waves [7,8]. This is allowed by the mathematical properties of the mass balance equations of chromatography which are very similar to those used in hydrodynamics and aeronautics. It is not intuitive to consider a concentration as a wave. Nevertheless, we should. The migration of a concentration in a band is not directly related to the propagation of matter, as lucidly explained by Helfferich and Peterson [23]. Matter and concentrations propagate at different velocities. Further illustrations of this fact were provided recently [13]. Concentrations can disappear at any time without violating a conservation principle. Thus, the migration of concentrations (considered separately from the migration of defined amounts of matter) has much to do with the propagation of waves. Those who are not familiar with these concepts should check Ref. [22] and pp. 227–228 in Ref. [12].

The concept of coherence and the coherence conditions are discussed in two sections of the following review. For a wave to be coherent, the wave velocities must be the same for all the components involved, at a given point in space and time (i.e., in the  $(z,t)$  space). Glueckauf [1,2] had to assume the existence of such a relationship in order to derive his analytical solution of the ideal model. Liu [24] showed that the coherence condition results from the mathematical properties [7,18] of hyperbolic systems of partial differential equations such as the set of multicomponent mass balance equations in the ideal model. Helfferich has generalized the concept of coherence, suggesting that it is a fundamental law of nature, independent of the form of the equations modeling the phenomenon (e.g., Huygen's pendulum). This deserves serious consideration.

The method of characteristics provides the trajectories of concentrations. These trajectories are conveniently studied by considering the distance–time diagram. Like waves, concentrations can propagate in disperse boundaries, similar to ordinary waves, and in shock waves. When the initial and final state of the chromatographic system are different constant concentrations (e.g., following the injection of a concentration step by pumping a constant concentration solution into the column initially filled with pure mobile phase), the profile consists of a concentration discontinuity (also called concentration shock or shock) or a diffuse boundary called a simple wave, depending on the direction, upward or downward, of the convexity of the isotherm.

The hodograph transform relates the concentrations of the two compounds along a chromatogram. Chromatographers are used to considering concentration profiles along the column and elution profiles which are the history of concentrations at the column outlet. The solution of the chromatographic problem requires the determination of the functions  $C_1(z,t)$  and  $C_2(x,t)$  which allow the derivation of concentration profiles along the column at any time or of the elution profiles for any column length. Instead we may want to consider the location  $z(C_1, C_2)$  where we can find the two concentrations  $C_1$  and  $C_2$  at the same time, or the time  $t(C_1, C_2)$  when they are

<sup>1</sup>Characteristics are called composition paths by Helfferich and Whitley [12].

located at the same place. Replacing the former set of functions ( $C_1(z,t)$  and  $C_2(z,t)$ ) by the latter one ( $z(C_1, C_2)$  and  $t(C_1, C_2)$ ) is performing the hodograph transform. To this transform is related the hodograph plot which consists in plotting  $C_1$  versus  $C_2$  in the elution chromatogram. When a diffuse boundary is found between two constant states (i.e., is a simple wave), its hodograph plot is a line. This line is easily derived from the isotherm and provides a convenient access to the band profiles. It is usually curved but it is a set of two straight lines in the case of competitive Langmuir isotherms.

The essential tools to understand non-linear chromatography are the coherence condition, the hodograph transform, the method of characteristics and the correspondence between the hodograph space and the physical space which is provided by this method. They all play a key role in the construction of solutions, i.e., of band profiles along the column or of chromatograms. Those interested in understanding the separation process in preparative chromatography have two options, the use of computer programs to calculate directly numerical solutions under given sets of conditions and the construction of the corresponding composition paths, distance–time diagrams and band profiles. While the former approach is the best for direct comparison between experimental and theoretical profiles (provided that the relevant thermodynamics and kinetics data are available), the choice is very much a matter of personal preference when one wants to understand the relationship between the equilibrium thermodynamics and the band profiles. Often, consideration of both approaches will turn out to be most informative.

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