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Introduction to the series "Non-linear waves in chromatography"

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ABSTRACT

The series of Reviews on "Non-linear waves in chromatography", to be published in this journal, is outlined.

We owe our very life to non-linearity. It is nature's non-linearity that makes all the complex phenomena possible that are needed to sustain a living organism, that has made our world what it is. The scientist and engineer of course know that, yet they love linear theories for the relative ease with which they lead to solutions and predictions. And once in a while an important field opens up in which the practitioner can indulge in the luxury of a linear theory without sacrificing essentials. Such a field has been analytical chromatography.

Non-linearity in chromatography arises from interactions between molecules of the same or different solutes. In analytical chromatography, the desire to work with smallest samples and attain highest separation efficiency has led to techniques working at extreme dilution and very low column loading. Solute molecules then rarely encounter one another, and so do not interact to any significant extent. Improvements in sorbents and stationary phases, in column design, and, most of all, in detector technology have made it possible to reduce sample size and column loading farther and farther, and so have kept moving analytical chromatography ever more deeply into the linear range. Only in the last few years has interest in chromatography as a *preparative* tool experienced a substantial revival. Here, the desire is for large througput and recovery at high concentrations, conditions under which solute interactions and thus non-linearity become prominent.

To be sure, there is nothing new about non-linear chromatography. From Tswett [1] to Tiselius [2] and Spedding [3], chromatography was used primarily for preparative separations. Only the enormous success of analytical liquid–liquid and gas–liquid chromatography in the 1950s changed that, making chromatography a method of chemical analysis almost by definition. In a way, we are now paying the price for the genius of A. J. P. Martin (see refs. 4 and 5), who conceived of analytical chromatography as we know it today and triggered the "gas chromatographic revolution" that made us forget much of the earlier work.

What the practical chromatographer today may wish to know about basic non-linear theory dates largely back to the years before 1970, a good deal of it to before 1955. However, this information is not easy to retrieve. One problem is that many of the bits and pieces do not seem quite to fit together as they stem from different fields of science, each of which had developed its own framework and viewpoints. Also, some of the essential work is highly mathematical, making it difficult to recognize the

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underlying physical reality. Lastly, not only had each field developed its own terminology, but it kept changing it as time progressed. Therefore one should not be surprised to see old ideas reinvented, usually being given new names that add to the confusion.

I have been asked by one of the editors of this journal, Dr. Lloyd R. Snyder, to attempt presenting a review of basic non-linear theory aimed at the practitioner rather than the theoretician, with an emphasis on understanding of cause and effect, and with a minimum of mathematics. Not being a practicing chromatographer myself and no longer having followed all recent developments, I agreed only after I had succeeded in persuading Dr. Peter W. Carr to act as my guide, contribute the essential perspective and direction, provide the expertise in current practical chromatography, and join me in formulating the analysis of the various facets. Moreover, Lloyd Snyder kindly offered to give our series more than just the routine editorial attention. Any credit for the series will be owed to all three of us, any blame must be mine alone.

The topics we intend to cover are:

Part I. Waves, shocks and shapes: single-solute, non-linear chromatographic waves, their velocities, and their sharpening or spreading tendencies; shocks and shock layers and their profiles; constant and proportionate patterns; and shapes of single-solute peaks in elution and bands in displacement.

Part II. Wave interference and coherence: column response in multicomponent systems; wave patterns; interference of waves generated by successive injections; the coherence concept; composition paths and distance–time diagrams; vacancy chromatography; gradient elution; and linear chromatography as limiting case of solutes at trace level.

Part III. Multicomponent Langmuir systems: ideal chromatography in systems with competitive Langmuir isotherms; simple mathematics for such systems, based on the ω- or h-transformations; analogy to ion exchange with constant separation factors; and transients in displacement development.

Part IV. Arbitrary multicomponent systems: with synergism; effects of selectivity reversals; non-isothermal systems; methods for multicomponent isotherm determination.

This agenda is flexible, and additional or alternative topics might suggest themselves or be suggested to us as we proceed. Mathematics will remain restricted to a few simple equations needed to understand effects and to some techniques that can give approximate answers in complex cases with minimal effort. As much as possible, a framework will be provided in which standard theories have their logical places and can be compared with one another, and a dictionary of equivalent terms will be compiled. Emphasis will be on conceptual understanding and practical utility rather than on derivations or interpretation of observations. Also, as much as possible, the instalments will be kept independent so that each can be read without detailed study of the others, in order to allow the reader to pick and choose.

Lastly, we claim no original authorship for the material to be presented. Almost all of it will be from previous work, much of it by others, and the few exceptions will be relatively insignificant. However, there will be no attempt to cover prior theories exhaustively. Rather, those will be chosen which best prove or illustrate the points to be made, and often reviews rather than first publications will be cited. We apologize ahead of time to all whose worthy contributions may go without mention.

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