

Chapter 1

Unified Chromatography: What Is It?

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In this chapter we explain why we are interested in this concept, give some of the history, introduce some of the topics to be treated in the subsequent chapters, and set the stage for much further consideration.

Today we are at an extremely exciting point in the development and refinement of chromatography. Researchers are recognizing that some of the perceived limits of the past are not real. We are using gases as mobile phases but compressing them until they have liquid-like properties. We are condensing what are ordinarily gases into liquids and using them as mobile phases at subambient temperatures where ordinary liquids are frozen solid. We are using ordinary liquids above their normal boiling points but still keeping them in the liquid state by the application of pressure. We are finding ways of reducing mobile phase viscosity, increasing diffusion rates, increasing analysis speed, tuning selectivity, and explaining retention more comprehensively. And we are removing the barriers that artificially distinguish and limit essentially similar chromatography techniques, thus opening new understanding and even more new possibilities. This is all included in the concept we call *unified chromatography*.

We are not sure how far the concept can be developed or what additional benefits may arise. In fact, the only thing we are really sure of is what unified chromatography is not. The antithesis of the concept of unified chromatography is the often accepted practice that the methods, instrumentation, and theories employed in any particular separation technique, for example gas chromatography, are completely unrelated to those used in other separation techniques like supercritical fluid chromatography, liquid chromatography, or electrophoresis.

We organized the symposium, from which this book was derived, to bring together people working with different aspects of chromatography. We wanted these people to consider the underlying similarities of their work, test the strength of the traditional boundaries separating chromatography into individual techniques, and help catalyze even more new work and understanding.

The concept of "One World of Chromatography" has been an intriguing, albeit somewhat ethereal, Holy Grail for chromatographers for decades. Different individuals have proposed the idea of a unified theory, others a single instrument,

while yet another group has advocated a single technique that would encompass all of the technology currently available.

Martire has been a major proponent of a unified approach to the theory of chromatography. He first used the words *unified theory* in the titles of a set of papers (1,2) published in the early 1980s. The models were based on a statistical mechanical treatment of the equilibrium distribution of a solute between the stationary and mobile phases in liquid chromatography. While the initial work involved only liquid chromatography, the effort was soon extended to include liquid, gas, and supercritical fluid chromatography (3-6). The most recently developed models are based on the lattice fluid model first proposed by Sanchez and Lacombe in 1978 (7,8) and subsequently enhanced by Sanchez and his colleagues (9-12). The lattice fluid models are complex, but currently represent the only extant theory that can be used to interpret, let alone predict, the retention volume of a chromatographic solute as a function of pressure, temperature, and mobile phase composition and/or density.

Analytical and physical chemists have long been using experimental results from phase distribution measurements to develop theoretical models to interpret retention volume data from chromatographic experiments. Chemical engineers have, in a similar manner, often used chromatographic results to describe the solubility of solids in supercritical fluids or mixtures of supercritical fluids and liquids in polymers. Shim and Johnston (13-15) studied the partition of toluene between fluid and polymeric phases. More recently, Eckert *et al.* (16) studied the effect of various modifiers, viz., methanol, acetone, and isopropanol, on the swelling of poly(dimethylsiloxane) caused by the absorption of modifier by the polymer over a range of temperatures and pressures. Eckert *et al.* (17) used the Sanchez-Lacombe lattice fluid model, the same basic idea used by Martire for his Unified Theory of Chromatography, to model the swelling, absorption, and isothermal phase behavior for the modifiers. Again, the lattice fluid models are complex, but their ability to describe such complex systems involving a solute, supercritical CO₂ and a polar liquid modifier, all in equilibrium with a polymeric stationary liquid phase, is quite remarkable and bodes well for our ability to develop a truly comprehensive theory for a hypothetical unified chromatography. The collaboration between chemists and engineers is encouraging and most certainly necessary for our further understanding of the fundamental mechanisms that control all types of separations.

There also has been a push to develop instrumentation that could be used in a unified approach to chromatography. Ishii and Takeuchi (18,19) used the titles *Unified Fluid Chromatography* and *Unified Capillary Chromatography* to describe their work on the development of a single chromatographic instrument that could perform GC-, SFC-, or HPLC-like separations depending upon the temperature and pressure of the mobile phase. Recently, many individuals and groups have espoused the same idea, but to our knowledge, Ishii's group was the earliest to use the word *unified* in the title of a published article describing multi-use chromatographic instrumentation.

In 1991, the late Professor J. C. Giddings published a well-received book entitled *Unified Separation Science* (20). The volume was meant to be a textbook for a graduate-level course in separations. However, the author took advantage of the privilege of authority to remind those of us who teach such courses or workshops that "...it is more important to understand how it works than how to do it; basics rather than recipes. Procedures will change and evolve and old recipes are soon obsolete, but the underlying mechanisms of separation will be around for a long time."

More recently, several authors have addressed the idea of unified chromatography rather than a particular implementation of the concept. In particular, Chester (21,22) has discussed what he calls "Chromatography from the Mobile Phase Perspective". He emphasizes the measurement and interpretation of phase diagrams of mobile phase fluids as a means of defining the chromatography and eliminating unnecessary boundaries between named techniques. The relation between the phase behavior of mobile phases and the resultant chromatographic performance of chromatographic systems is a fundamental relationship that is often overlooked. The primary reasons for such neglect are the experimental difficulty involved in the determination of phase diagrams, especially when binary or ternary fluids are considered, and the somewhat arcane nature of phase diagrams in general.

We have based these introductory comments on a few of the chromatography publications where the term *unified* was mentioned; however, it is obvious that myriad publications could be cited in an effort to eliminate the artificial barriers established historically between the various forms of chromatography or separation schemes in general. Most of the so-called two-dimensional chromatography schemes can be viewed as progress toward a single, combined form of chromatography. And, finally, almost all of the papers presented at the Symposium, as well as the chapters appearing in this volume, present cross-cutting, state-of-the-art research by some of the old-timers and new-comers in the field of separation science. If these presentations and articles help to eliminate some of the prejudice and tunnel vision evident in the chromatographic literature, then we will have fulfilled a portion of our original goal in opening for discussion the alluring concept of *unified chromatography*.

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