

Unified Chromatography

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Emerging chromatographic schemes involve binary mobile phases with CO₂.

Chromatographic methods are usually classified according to the physical state of the mobile phase—for example, GC, supercritical fluid chromatography (SFC), and LC. This admittedly oversimplified classification scheme exists partly because of the similarity of most chromatographic stationary phases, which are usually either polymers or solid adsorbents and are often deactivated by some chemically bonded moiety. Because of the banality of stationary phases, any attempt to unify the various forms of chromatography will naturally center on the mobile phase. To date, many researchers consider the most promising approach to unification to be the use of CO₂ as the mobile phase, because of the “tunable” solvent strength of this fluid.

Unfortunately, neat CO₂ alone is not a good mobile phase because of its poor solvent properties. For this reason, a polar, organic “modifier” is usually mixed with CO₂ to produce a mobile phase with improved solvent properties for polar solutes without significantly altering the physical properties of the mobile phase. The development of practical chromatographic schemes involving binary mobile phases with CO₂ as a component is a promising area of research, and analytical applications of this technology constitute a significant body of chromatographic literature. These systems, although chromatographically useful and interesting, are also very complex, difficult to control experimentally, and often intractable to theoretical modeling and interpretation. For these reasons, a broad discussion of these fasci-

ating systems is both timely and appropriate.

The normally assigned role of the mobile phase in any chromatographic system is simply to transport the solutes through the column. The classical model assumes that all solutes in the mobile phase travel at the same velocity as the bulk mobile phase itself. There are exceptions to this simplistic model, such as size-exclusion and hydrodynamic chromatography, in which various regions of the mobile phase travel at different velocities. Nevertheless, assuming that all of the solutes spend the same amount of time in the mobile phase, any observed chromatographic resolution of the solutes must be determined solely by the amount of time each solute resides somewhere in the column other than in the mobile phase.

This concept illustrates the normal role of the so-called stationary phase. If molecular diffusion is neglected, the stationary phase provides a place in the column for the solutes to reside without undergoing axial movement. Researchers, however, should keep in mind that not all the stationary-phase components must be fixed within the column. In addition, not all of the mobile phase must move at a uniform velocity. The analytical solutes may interact with mobile-phase components, stationary-phase components, or mobile-phase components dissolved in or adsorbed on the stationary phase.

Binary Mobile Phases

Binary mobile phases are used often, particularly in HPLC and SFC. Some very elegant separations have also been achieved with gradient elution and solvent programming techniques. Such multicomponent mobile phases are popular primarily because they can be used to provide continuous control of the

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