Liquid Chromatography Problem Solving and Troubleshooting

Question

What causes column voiding and is there any way of preventing or minimizing it from occurring? Also, I am curious as to why some bonded phases have better performance in terms of voiding over others?

Answer

Unfortunately, voiding is the result of natural aging processes of a column that arise from the chemical, physical, and mechanical instability of the packing material under various operating conditions. Depending on the type of column, voiding and physical volume changes in the packed bed can be influenced by various eluent conditions as well as temperature and pressure.

For chemically stable materials such as those commonly used as size-exclusion packings manufactured from polystyrene-divinylbenzene copolymers, the most common cause of physical changes in the bed is the improper use of organic solvents as eluents. An increased resistance to flow and a decreased bed volume result from the swelling and shrinking of the polymer, respectively. The amount of change in a polymer's solvated volume is dependent on the type of solvent used and the degree of crosslinking in the polymer. Even though some of the highly crosslinked packings are mechanically robust, they still swell and shrink depending on the eluent's interaction with the polymer. To minimize problems associated with changes in the bed's volume, it is important to follow the manufacturer's recommendations in terms of the eluent conditions.

For reversed-phase packings that are based on the chemical modification of porous silica, the pH of the eluent and the operating temperature of the column can dramatically affect column stability. A practical working range for most silica-based materials is a pH level of 3 to 8.5. Alkaline eluent conditions are especially problematic, because silica is readily soluble in basic aqueous solvents. Likewise, the chemical instability of the siloxane bonds (that attach the bonded phase to the surface) and the solubility of the underlying silica particles increase at elevated temperatures. When column breakdown occurs, it proceeds by a 3-step process that involves phase loss, hydrolysis of the underlying silica matrix, and finally mechanical collapse of the porous substrate's structure. Initially, phase loss results in slowly decreasing solute retention and increasing peak asymmetry. In the final stages, mechanical breakdown of the substrate leads to the formation of channels and the collapse of the packing material. The manifestation of this process is column voiding and the formation of erratic peak shapes.

A number of manufacturers have attempted to increase the lifetime of reversed-phase packings by preparing chemically modified surfaces with short bulky groups near the point of chemical anchoring. An example of this type of approach is the preparation of monomeric octyl phases using di-isopropyloctylchlorosilane instead of the more traditional use of dimethyl-octylchlorosilane. This technique works to extend column lifetime by sterically protecting the underlying silica surface. A further advantage of these types of phases is that they show improved peak symmetry toward problematic compounds such as amines by blocking residual silanols. Even with improved bonding techniques, it is not theoretically possible to completely protect the surface, because silica is an amorphous heterogeneous material.

Because the initial stages of voiding for silica-based materials is related to the chemical instability of the packing, eluent conditions that minimize these problems increase column lifetime. Likewise, chemical instability is a time-dependent process, and when not in use, the appropriate storage of reversed-phase materials with more chemical-friendly solvents can also help extend their life.

The purpose of *Chromatography Problem Solving and Troubleshooting* is to have selected experts answer chromatographic questions in any of the various separation fields (GC, GC–MS, HPLC, TLC, SFC, HPTLC, open column, etc.). If you have questions or problems that you would like answered, please forward these to the *Journal* editorial office with all pertinent details: instrument operating conditions, temperatures, pressures, columns, support materials, liquid phases, carrier gas, mobile phases, detectors, example chromatograms, etc. In addition, if you would like to share your expertise or experience in the form of a particular question accompanied by the answer, please forward to JCS Associate Editor, *Chromatography Problem Solving and Troubleshooting,* P.O. Box 48312, Niles, IL 60714. All questions/answers are reviewed to ensure completeness. The *Journal* reserves the right not to publish submitted questions/answers.

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