Gas Chromatography Problem Solving and Troubleshooting

Question:

Occasionally, one of my capillary columns degrades faster than usual. In terms of the GC system and method, nothing has been changed. Why does this occur? Do column lifetimes vary tremendously between columns?

Answer:

There are a number of factors that influence column life. There should not be a large variation in column life between columns of the exact same description from the same manufacturer. This is true provided that nothing has changed with the GC system, methods, column temperatures, or samples. Unfortunately, it is change in one of these areas that is usually responsible for premature degradation.

The most common source of column life variability is probably changes in the samples. In many cases, these changes are not apparent in the chromatogram or on visual inspection of the samples. The same types of samples can be analyzed for years without any problems. However, if a sample unexpectedly contains poorly volatile or nonvolatile compounds (e.g., polymers, salts, proteins, solid particles), these compounds can contaminate the column. The poorly volatile or nonvolatile compounds in the sample accumulate in the column. They coat the interior of the column and interfere with the proper partitioning of the sample compounds into the stationary phase or interact with the sample compounds. This results in peak shape problems, such as tailing or broadness, or baseline problems, such as wander and drift. The concentration of the contaminants and the number of sample injections determine the severity and timing of potential chromatographic problems. A few samples that contain a low concentration of the contaminants will cause few, if any, problems. Even two to three injections of a highly contaminated sample can rapidly degrade the performance of the column. Sample contamination with nonvolatile compounds is often outside the control of the analyst; thus, it is not the result of an analytical mistake or an error by the GC operator. Sometimes, nonvolatile compounds are not in the actual sample but may originate from something that has come in contact with the sample during preparation (e.g., vials, caps, septa, solvents, pipettes).

Nonvolatile compounds usually accumulate in the very front portion of the column. This is the reason that trimming the front of a column often restores its performance. When columns become contaminated with residues, it is a common practice to "bake out" the column at a high temperature. Although this removes most of the poorly volatile compounds, all of the nonvolatile compounds remain in the column. Solvent rinsing the column is usually required to remove the poorly volatile or nonvolatile compounds that can migrate several meters into the column. Often a high-temperature bake out can make the problem worse by causing the poorly volatile or nonvolatile compounds to decompose or polymerize. This often makes them insoluble in organic solvents and water, thus they cannot be removed by solvent rinsing the column. The column is now permanently contaminated and often unusable.

Column damage or degradation can also be related to other contaminants in the sample. Mineral acids and bases rapidly damage polysiloxane and polyethylene glycol based capillary columns. Acids such as sulfuric, nitric, phosphoric, and chromic, and bases, such as sodium and potassium hydroxide, are particularly damaging to columns. These compounds are highly retained by most columns, thus the acid or base is focused at the front of the column. If the column is used at higher temperatures, these acids or bases may spread over an appreciable length of the column. Usually, trimming 0.5–2 m from the front of the column removes the damaged portion and restores column performance. If a strong acid or base is needed in the sample, hydrochloric acid or ammonium hydroxide cause the least amount of damage due to their higher volatilities. Organic acids and bases such as acetic acid or triethylamine are even better.

The next most common cause of rapid column degradation is a carrier gas leak. A leak allows air to enter the column. Oxygen is damaging to stationary phases at high temperatures. At room temperature, oxygen does not damage a column; however, the amount of damage significantly increases as the column temperature increases. The most common source of leaks is the injector (e.g., septum, fittings) or the gas lines coming from the gas supply. Even a tiny leak can introduce enough air to result in column damage each time the column temperature is raised. A higher oxygen level in the carrier gas can also contribute to faster-than-normal column degradation. A lower-grade gas or expired oxygen trap are common sources of higher carrier gas oxygen levels. Polar stationary phases are especially susceptible to oxygen-induced damage. In general, polar stationary phases have shorter lifetimes than nonpolar stationary phases.

The symptoms of a column that has been damaged by oxygen are excessive column bleed, activity, or loss of resolution (due to peak broadening). Usually, excessive column bleed is the first noticeable symptom. If the column is not heated to temperatures approaching its upper temperature limit, higher-than-normal column bleed may not be

evident. Column activity results in peak tailing or size loss for active compounds. Most active compounds contain hydroxyl or amine groups. Hydrocarbons, halocarbons, and ethers are not active. Most esters, ketones, and aldehydes are rarely active; sometimes they may decompose in the hot injector or column. Noticeable peak broadening or tailing may occur when a column is severely damaged. This problem usually occurs after the onset of excessive column bleed or activity. Again, depending on the analysis conditions and compounds, column bleed and activity may not be directly evident.

If a substantially shorter column lifetime is experienced, it is almost always due to a change in the GC system or sample. Poorly volatile or nonvolatile sample compounds, the presence of mineral acids or bases, a leak in the GC, or exposure of the column to higher-than-normal temperatures all reduce expected column life. Investigation of these areas should be undertaken if column lifetimes become shorter than usual.

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.

Dean Rood
Associate Editor