

Gas Chromatography Problem Solving and Troubleshooting

Question:

I have been experiencing a problem with erratic retention times for a capillary alumina column. The retention time shifts are not the same for each compound, but they all become longer. The problem seems to appear and disappear at random. The carrier gas linear velocity is correct and stable, and the problem does not occur for other types of columns used in the same GC. Peak resolution is sometimes reduced due to the change in the relative retention of closely eluting peaks. What is causing this problem?

Answer:

The retention time for a specific compound is dependent on the stationary phase, column dimensions, column temperature, and carrier gas average linear velocity. Because the linear velocity has been verified as correct and other columns in the GC are fine, the problem is probably not directly related to the GC. The same column has been used; thus a change in the column dimensions can be eliminated as a cause. This leaves the stationary phase as the source of the retention time shifts. Because the retention times sometimes return to their original values and the occurrence of the problem is erratic, it is unlikely that there is any stationary phase damage. Substantial damage to the stationary phase would be required before significant retention shifts would occur, and the problem would continue to become worse over time. The only reasonable cause left is a temporary alteration of the stationary phase by some unknown event or substance. Contamination of the column by a highly retained substance or a sample compound present at a high concentration are the most probable causes.

Erratic retention times for alumina columns are not unusual. Fortunately, the most common cause of this type of problem is understood and easily reversible. alumina adsorbs water, which affects retention times. As more water accumulates in the column, the retention times shift by a larger amount. Retention time shifts approaching 50% have been reported for hydrocarbons chromatographed in a water-saturated alumina column. If the alumina column is held at a high temperature such as 200°C, the water slowly elutes from the column. Unfortunately, eight or more hours is often needed to remove all the retained water. The effect of water on alumina explains the retention time stability problem. The randomness of the problem can be rationalized by the differences in the amount of water in the injected samples, the number and timing of sample injections, and the frequency and duration of column heating. Trace levels of water in the carrier gas may also contribute to the buildup of water in the column. Whenever the alumina column is exposed to higher temperatures, especially for prolonged time periods, the water is removed from the column. This explains the occasional return to the original retention times. As more samples are injected and volumes of carrier gas flow through the column, water starts to accumulate in the column, and the retention times begin to shift once again. Carbon dioxide is also adsorbed by alumina, but it does not seem to affect retention time stability.

Adding a short, high-temperature bake-out to the end of each GC run eliminates the retention time instability problem with alumina columns. Though this adds a few minutes to each run, it is the best and easiest method to prevent an accumulation of water in the column. Maintaining as leak-free a GC as possible, using moisture traps for the carrier gas, and minimizing the amount of water in the sample reduces the onset and severity of the retention time instability problem. Some alumina columns are more susceptible to water-induced retention shifts and require different amounts of heating before all of the water elutes. The type of salt or additive used with the alumina influences the susceptibility of the column to the effects of water. Because column manufacturers often use different salts and additives, the source of the column also influences the overall affect of water on an alumina column.

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