

Gas Chromatography Problem Solving and Troubleshooting

Question:

Occasionally I experience a shift or change in my retention times. Sometimes the retention times change and remain at the new values, and in other instances the retention times are inconsistent. What is causing this problem?

Answer:

There are a large number of parameters that affect retention time. The first step in solving a retention time problem is to determine whether the change fits any type of pattern. Are all or only some of the peaks affected? Do the peaks shift in the same direction? Do they shift by the same amount? The presence of a pattern (or lack of one) can often narrow the number of possible causes.

If all the peaks shift in the same direction, the possible causes are a change in the column temperature, column dimension, or carrier gas average linear velocity or flow rate. If all the retention times shift by the same amount (within 0.05 min), the problem is caused by a change in the carrier gas velocity. Slower velocities increase the retention time, whereas faster velocities decrease the retention time. If there does not appear to be a change in the velocity or flow rate, there may be an error in the original or current measurement. Setting the velocity or flow rate at a different column temperature or a calculation mistake (e.g., incorrect equation, units, column length) are the typical carrier gas errors. In rare cases, a faulty flow controller or pressure regulator may cause inconsistent carrier gas velocities or flow rates. A change in a column dimension causes a shift in the retention times, but the amount of the shift is different for each peak. The amount of the shift increases with increasing retention times. Higher retention times are obtained with increases in column length and stationary phase film thickness and decreases in the column diameter (providing no other parameter has changed). Changes in film thickness cannot be visually determined, and small changes in length and diameter are very difficult to directly observe. Confirming the identity of the column is the best method to track down this type of problem. Keep in mind that column length often decreases with use due to trimming or cutting of the column with installation or maintenance. A change in the column length or diameter may also result in the setting of the incorrect carrier gas velocity or flow rates, thus compounding the problem.

A change in the temperature program often causes a retention time shift of all the peaks. A change in the initial temperature, the initial hold time, or the ramp rate can affect all of the peaks. Retention times increase with a lower initial temperature, longer initial hold time, or a slower ramp rate. Depending on the temperature program, some types of program changes only affect the later eluting peaks. If all the peaks after the first one exhibiting a retention time change are affected, a change in the temperature program is the usual cause. If the change in the temperature program occurs in a later portion of the program, only the peaks eluting after this change are affected. For example, if the program starts with a 5-min hold at 50°C, a change in the ramp only affects the peaks with retention times greater than 5 min. If all the peaks shift in the same direction but one pair seems to reverse in elution order, an unusual effect called a peak inversion may have occurred. This is uncommon, but combinations of column stationary phase, compounds, and temperature conditions are more susceptible (but still fairly hard to predict) to this effect. If there is a pronounced change in the peak order, a column with a different stationary phase is being used. Also, determine whether there are any changes in the sample (e.g., incorrect sample or decomposition).

If only one or very few peaks in a chromatogram exhibit a retention time change, there are several possible causes of this type of problem. A large concentration change of a compound in the sample may result in a change in the corresponding peak's retention time. In some cases, this concentration change may also cause a small retention time shift of the adjacent peaks. A change in the sample solvent may be responsible for a retention time shift; however, only the

peaks eluting closest to the solvent front are affected. The retention time shift increases the closer the peak is to the solvent front. A sample-solvent-induced retention time change is often accompanied by a change in the peak shape. For samples containing a significant portion of the matrix, an interfering peak coeluting with an analyte peak may cause a small change in the apparent retention time. The peak often appears to be broader and sometimes slightly asymmetric.

For GCs with a backpressure-regulated injector, a leak in the injector often results in a retention time shift. Usually there is a decrease in the retention times by the same amount for all the peaks. Sometimes the size of the shift is erratic and changes from injection to injection. If the size and direction of the retention time shift changes with each injection, a leak in the septum due to numerous injections (and not from a loose septum nut or fitting) is the usual cause. Regardless of the type of injector, it is best to measure or calculate the carrier gas average linear velocity or flow rate. The reading on the head pressure gauge can be incorrect if there is blockage in a gas line or a faulty component in the flow system.

The column oven may drift out of calibration as the GC ages. This means that the actual oven temperature is different than the one shown on the display. Some GCs can be recalibrated by the user as long as an accurate temperature probe is available. Some GCs require a qualified service engineer to perform the recalibration. Consult the GC's instruction manual for details.

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