Gas Chromatography Problem Solving and Troubleshooting

Question:

Some of the earlier-eluting peaks in my chromatogram are broad and tailing. Also, the solvent front interferes with the first peak. I have tried changing the temperature program, carrier gas flow rates, and injection volume. None of these changes improved the peak shapes. Is there anything else that can be done to improve the peak shape?

Answer:

The cause of the peak shape problem is related to the split ratio. A 1:5 split ratio is being used, which is too low for a 0.25-mm i.d. column (Figure 1A). The split ratio is calculated by dividing the column carrier gas flow rate into the split vent flow rate. This value is the relative amount of carrier gas flowing out of the split vent compared with the column flow rate. For example, a 1:5 split ratio means that 5 times the amount of carrier gas is flowing out of the split vent in comparison with the column. If the sample in Figure 1A is run using a 1:50 split ratio, the peak shape problem is eliminated (Figure 1B). In addition, the size of the solvent front is reduced. The lowest split ratio that can be used is primarily dependent upon the diameter of the column.

The sum of the split vent and column flow rates is equal to the carrier gas flow rate through the injector. Typically, a minimum of 10 mL/min of total carrier gas flow rate is needed to obtain good peak shapes. Total flow rates of 20 mL/min and higher are recommended and provide the best overall results. The actual minimum is often influenced by the column temperature, sample compounds and solvent, volume of the liner, injection volume, and column. As the column diameter changes, so does the split ratio where 10 mL/min of total flow rate is obtained. For example, the helium flow rate for a 0.25-mm i.d. column is typically around 1 mL/min. A minimum split vent flow rate of 9–10 mL/min would be required, resulting in a split ratio of approximately 1:10. The helium flow rate for a 0.53-mm i.d. column is typically around 4 mL/min. A split vent flow of 6–7 mL/min would be required, resulting in a split ratio of approximately 1:1.5. Minimum split ratios for the various column diameters can be found in Table I.

When the split ratio is too low, the flow rate through the injector is very low and a long time is required to transfer the sample into the column. Some of the first compound molecules in the column may begin to move down the column while there are portions of the same compound's molecules still in the injector. If this occurs, the corresponding peaks will usually broaden, because the compound molecules are eventually spread out over a long length of column. The earliest-eluting compounds are the most susceptible to this behavior because they are the least retained by the column. This is seen in the chromatogram in Figure 1A. The later-eluting peaks are often not affected. The compounds corresponding to these peaks are more strongly retained by the column. The first molecules of these compounds that enter the column do not move down the column until a higher column temperature or longer time is reached. By the time the first compound molecules begin to

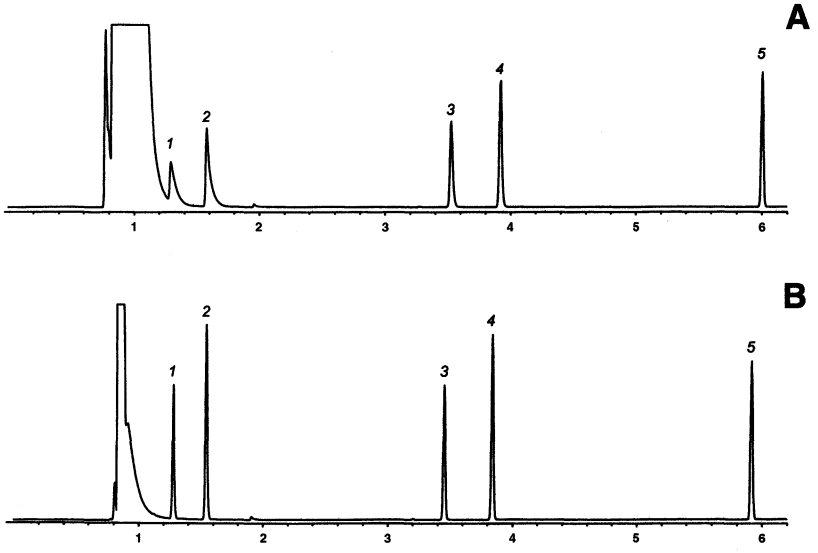

Figure1. Chromatograms at 1:5 split ratio (A) and 1:50 split ratio (B). Chromatographic conditions: column, DB-1 15 m x 0.25-mm i.d. (0.25-µm film thickness); split injector, 250°C; FID detector, 300°C; carrier gas, helium at 30 cm/s; column temperature, 60°C (1 min) to 180°C at 20°C/min. Peaks: 1, *n*-heptane; 2, toluene; 3, *n*-decane; 4, *n*-butylbenzene; 5, *n*-tridecane; 6, biphenyl.

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

Table I. Lowest Recommended Split Ratios

Column diameter (mm)	Minimum split ratio
0.18–0.20	1:20–1:25
0.25	1:15–1:20
0.32	1:10–1:12
0.53	1:3–1:5

move down the column, all of the compound molecules have been transported into the column and there are none remaining in the injector. All of the compound molecules are focused in a narrow band at the front of the column, resulting in a narrow peak. The severity of the peak broadening decreases as the retention of the corresponding compound increases. In some cases, all or none of the peaks will be broadened if the split ratio is set too low.

Split ratios above 1:100 are rarely used for column diameters of 0.25-mm i.d. or larger. Peak shape improvements are seldom obtained when split ratios above 1:100 are used. However, higher carrier gas consumption occurs with higher split ratios. For example, a 0.25-mm i.d. column set at a split ratio of 1:50 uses about 50 mL/min of helium, while a split ratio of 1:100 uses about 100 mL/min. Using the 1:50 split ratio consumes half the volume of carrier gas per minute, thus cutting the total cost of helium in half as well. Lower split ratios introduce more sample into the column. To minimize carrier gas costs, use the lowest split ratio that does not overload the column. Excessively high split ratios increase costs without any real performance benefits.