Gas Chromatography Problem Solving and Troubleshooting

Question:

At an initial temperature of 70°C for my temperature program, the earlier-eluting peaks in my chromatogram are poorly formed. At an initial temperature of 50°C, the peak shapes are fine (Figure 1). What is the problem?

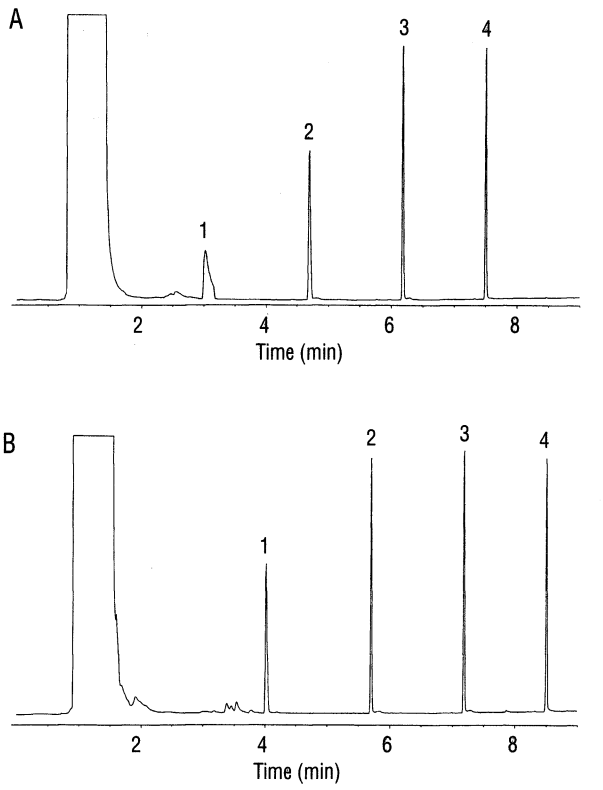

Figure 1. Conditions: column, DB-1 (15 m x 0.25-mm i.d., 0.25-µm film); injector, splitless (250°C, 0.5-min purge activation time); detector, FID (300°C); carrier gas, helium (30 cm/s); oven, (A) 70°C for 1 min, 70–210°C at 20°C/min (B) 50°C for 1 min, 50–210°C at 20°C/min. Peaks: 1 *n*-decane; 2, *n*-dodecane; 3, *n*-tetradecane; 4, *n*-hexadecane.

Answer:

The primary reason for the poor peak shape at an initial temperature of 70°C is a violation of the solvent effect rule for splitless injections. Splitless injectors are very inefficient at transferring the vaporized sample into the column. It is a slow process; therefore, the sample becomes spread over a wide region at the front of the column. This leads to broad or misshapen peaks. The solvent effect is used to focus the sample into a tight band at the front of the column. This results in properly formed peaks of acceptable width and shape. The solvent effect occurs when the initial oven temperature is around 10°C or below the boiling point of the sample solvent. After the sample solvent vaporizes in the injector, it is transported into the column by the carrier gas. Upon entering the column, the solvent condenses and forms a thick film, coating the walls of the capillary tubing. The sample analytes follow the solvent into the column and are trapped in the solvent film. Upon subsequent heating of the column (oven), the solvent vaporizes and leaves the analytes in a tight band at the front of the column. This results in narrow, symmetrical peaks. The sample solvent for the chromatograms in Figure 1 is *n*-hexane, which has a boiling point of 69°C. At an initial oven temperature of 70°C, the solvent effect does not occur, and the sample is not properly focused. This causes the poor shape of the first peak. At 50°C, the solvent effect occurs, allowing the good shape for the first peak. Since the solvent effect is necessary for splitless injections, the general rule is to use an initial oven temperature 10–30°C below the boiling point of the sample solvent.

The last three peaks in the 70°C initial temperature chromatogram (Figure 1A) are narrow and symmetric, even though there is a solvent effect violation. Why does this happen? The solvent effect can be violated for one set of conditions. If the boiling point of an analyte is about 150°C or greater than the initial column temperature, the solvent effect is not needed. The analyte focuses at the front of the column without the presence of a solvent film. The boiling point of *n*-dodecane (peak 2) is 216°C. This is 146°C higher than the initial column temperature. Cold trapping is occuring; however, it does not fully focus the peak. Note that the peak width is slightly thinner for the 50°C chromatogram (Figure 1B), in which the solvent effect occurred. For this compound, some solvent effect is still required to obtain full focusing of the sample band. The last two compounds have boiling points of 253°C and 287°C. These two compounds are fully focused at 70°C because their boiling points are much greater than 150°C above the initial column temperature.

Since column-temperature-dependent focusing is required for splitless injections, there are several situations to avoid if possible. Mixed sample solvents can be a problem, especially if their boiling points or polarities are quite different. Mixed polarity solvents can cause peak shape problems, especially if some of the analytes are substantially more soluble in one solvent than in the other. When using mixed boiling point sample solvents, the initial column temperature has to be 10–30°C below the lowest boiling solvent. If the higher boiling solvent is more than 10–20% of the total solvent, any peaks that elute between the solvent peaks may exhibit poor shapes. Finally, any peaks that elute before the solvent front are often very broad and rounded. This requires that the solvent peak elute before any analyte peak of interest. Splitless injections require specific temperature conditions to obtain good results. If these conditions are not met, poor peak shapes are often obtained.

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