Gas Chromatography Problem Solving and Troubleshooting

Question:

I installed a 1-m × 0.53-mm-i.d. guard column on the front of a 0.10-mm-i.d. capillary column. Upon injecting methane to set the average linear velocity, I noticed that the methane peak was very broad and eluted much later than expected (Figure 1A). The peaks in a test mixture were also broad (Figure 1B).

I reinstalled the guard column several times with the same results. Upon removing the guard column, acceptable methane and test mixture peaks were obtained, and the retention times were much shorter (Figure 2). Why did the guard column cause such a large increase in peak width and retention time?

Answer:

The peak broadening and retention time increase is caused by the difference between the carrier gas flow rate in the guard column and the 0.10-mm-i.d. analytical column. At 125°C with a carrier gas head pressure of 30 psig, the flow rate at the entrance to the 0.10-mm-i.d. column is approximately 0.17 mL/min. The pressure drop across 1-m × 0.53-mm-i.d. tubing at 30 psi is negligible; thus, the flow rate in the guard column is also 0.17 mL/min. The volume of a 1-m × 0.53-mm-i.d. piece of tubing is approximately 0.22 mL. Based on these values, the dead time (i.e., the time for a nonretained compound to travel through a column) in the guard column is about 1.3 min, which translates into an average linear velocity of 1.3 cm/s. A large amount of longitudinal diffusion occurs at such a slow velocity, allowing the sample band to broaden by a large amount. This causes the peak broadening evident in Figure 1. The slow carrier gas flow rate in the guard column is also responsible for the increase in retention time. The retention time increase is equal to the guard column dead time. The retention times in Figure 1B are about 1.3 min longer than those in Figure 2B.

One solution to the peak broadening problem is to use a guard column with a smaller diameter. The volume is

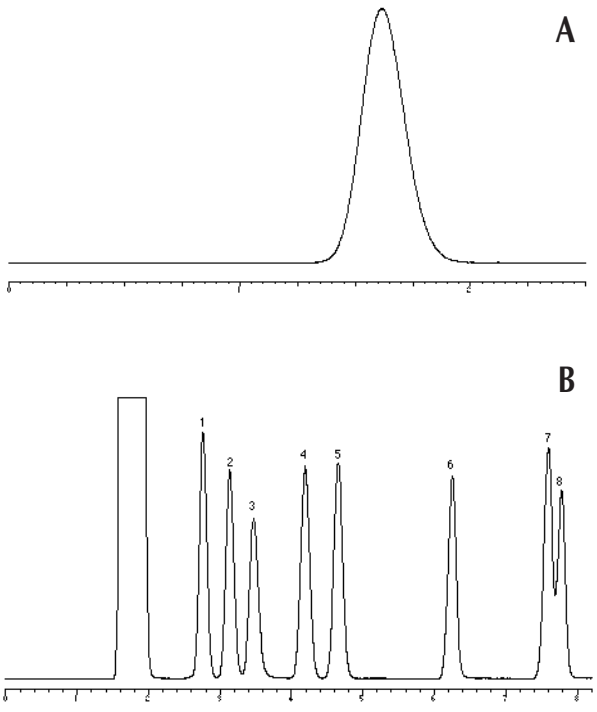

Figure 1. Chromatograms of methane (A) and a test mixture (B) with a guard column installed. Conditions: column, DB-1 (7 m × 0.10-mm i.d., 0.4-µm film thickness); guard column, 1 m × 0.53-mm i.d.; split injector, 250°C, 500:1 split ratio; FID detector, 300°C; carrier gas, helium at 30 psig; column temperature, 125°C. Peaks: 1, *n*-decane; 2, 1-octanol; 3, 2,6-dimethylphenol; 4, 2,6-dimethylaniline; 5, naphthalene; 6, 1-decanol; 7, *n*-tridecane; 8, methyl decanoate.

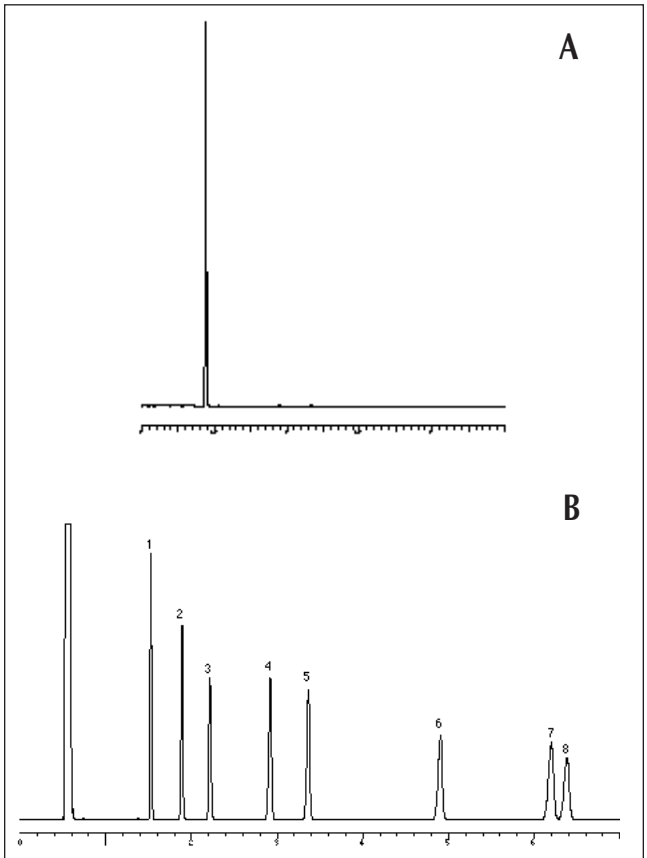

Figure 2. Chromatograms of methane (A) and a test mixture (A) without a guard column. Chromatographic conditions and peaks are the same as in Figure 1.

approximately 0.08 mL for a 1-m × 0.32-mm-i.d. piece of tubing and approximately 0.05 mL for a 1-m × 0.25-mm-i.d. piece of tubing. This reduces the dead time to approximately 0.45 and 0.30 min, respectively. Noticeably less peak broadening is obtained with these smaller diameter guard columns. Even when using small-diameter tubing, guard column lengths have to remain short when connected to 0.10-mm-i.d.analytical columns. A 4-m piece of 0.25-mm-i.d. tubing has approximately the same volume (and therefore dead time) as a 1-m piece of 0.53-mm-i.d. tubing.

Sometimes a 0.53-mm-i.d. guard column is used with small-diameter analytical columns so that on-column injections can be made using a standard 26-gauge syringe needle. In these cases, keeping the guard column fairly short minimizes the amount of peak broadening. A 10-cm × 0.53-mm-i.d. guard column has a volume of approximately 0.02 mL, resulting in a dead time around 0.13 min (0.17 mL/min carrier gas flow rate). A 0.13-min dead time results in only a very small amount of peak broadening and retention time increase.

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