Gas Chromatography Problem Solving and Troubleshooting

Question:

For several of my analyses, I cannot find the best avearge linear velocity for the carrier gas. A velocity that provides the best resolution for one set of peaks is not optimal for another. How do I determine the best average linear velocity in this type of situation?

Answer:

When compounds elute over a wide retention time range, the optimal average linear velocity ($\bar{u}$) for the earlier-eluting compounds is often different from the later-eluting compounds. Differences in optimal velocities depend on the carrier gas, columns dimensions, compound retention factors (k; formerly called the partition ratio), and the column temperature program. Sometimes the differences are small; in other cases, the differences can be quite large. This makes it difficult to accurately predict the optimal average linear velocity for a method without a small amount of experimentation.

One technique for determining the best overall average linear velocity requires analyzing the sample at several different velocities. Usually, velocities differing by 4–5 cm/s are sufficient. After the chromatograms are obtained, the resolution number for the closest-eluting or most important peaks is then calculated using the equation

$$R = \frac{tr_1 - tr_2}{Wh_1 + Wh_2} \qquad \text{Eq 1}$$

where tr_1 is the retention time of the first peak, tr_2 is the retention time of the second peak, Wh_1 is the width at half-height (in min) of the first peak, and Wh_2 is the width at half-height (in min) of the second peak. The resolution numbers can be compared to determine the velocities where maximum resolution is
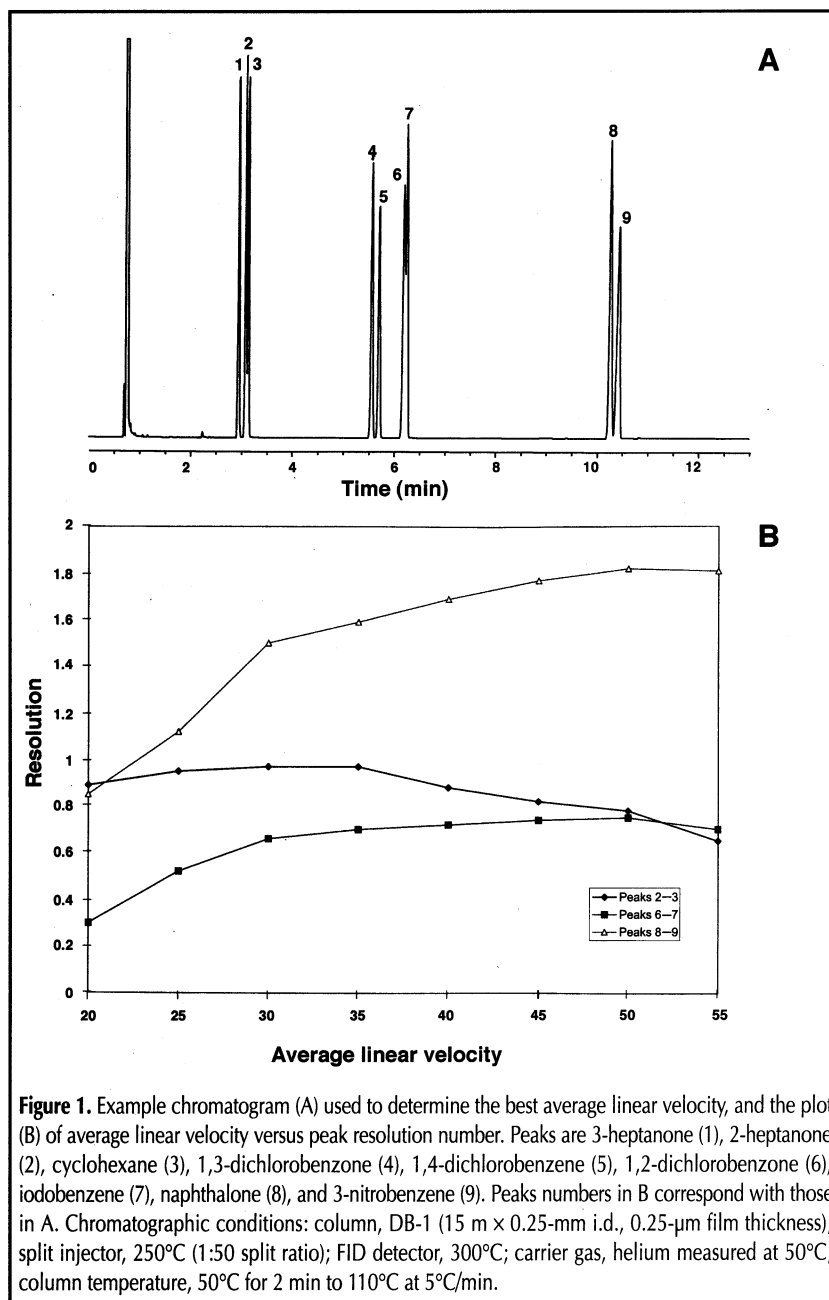

Figure 1. Example chromatogram (A) used to determine the best average linear velocity, and the plot (B) of average linear velocity versus peak resolution number. Peaks are 3-heptanone (1), 2-heptanone (2), cyclohexane (3), 1,3-dichlorobenzone (4), 1,4-dichlorobenzene (5), 1,2-dichlorobenzone (6), iodobenzene (7), naphthalone (8), and 3-nitrobenzene (9). Peaks numbers in B correspond with those in A. Chromatographic conditions: column, DB-1 (15 m × 0.25-mm i.d., 0.25-µm film thickness); split injector, 250°C (1:50 split ratio); FID detector, 300°C; carrier gas, helium measured at 50°C; column temperature, 50°C for 2 min to 110°C at 5°C/min.

obtained for each set of peaks. Plotting the average linear velocities versus the resolution numbers is often the most graphic and easiest comparison method.

Figure 1 shows an example chromatogram and the plot of resolution numbers for this sample for an average linear velocity range of 20 to 55 cm/s. For peaks 2 and 3, maximum resolution is obtained at an average linear velocity of 30–35 cm/s. For peaks 6 and 7 and peaks 8 and 9, maximum resolution is obtained at a velocity of 50 cm/s. At average linear velocities above 40 cm/s, there is a noticeable loss in resolution for peaks 2 and 3. This illustrates the common occurence where a single average linear velocity may not be optimal for all of the compounds in the sample. In this example, 50 cm/s is best for two sets of peaks, while 35 cm/s is best for another set.

Selecting the best overall average linear velocity usually involves deciding which set of peaks needs to be resolved by the

largest amount. The plot in Figure 1 is an example of this type of situation. If the resolution of peaks 2 and 3 is the most mportant, an average linear velocity of 35 cm/s is the best choice. Velocities above 35 cm/s result in lower resolution of peaks 2 and 3; velocities below 35 cm/s result in much lower resolution of peaks 6 and 7 and peaks 8 and 9. A velocity of 35 cm/s provides the best resolution of peaks 2 and 3 while sacrificing the smallest amount of resolution for the remaining peaks. If the resolution of peaks 6 and 7 were the most important, an average linear velocity of 50 cm/s would be the best choice. This would also be the best velocity for peaks 8 and 9. There is a large reduction in resolution for peaks 2 and 3 at 50 cm/s; therefore, it has to be decided whether a large resolution loss for peaks 2 and 3 is acceptable.

When the optimal average linear velocities differ by a large amount, a compromise is usually necessary. When considering all of the peaks in Figure 1, an overall compromise would be an average linear velocity of 35–40 cm/s. A velocity in this range maximizes the resolution of all three sets of peaks without favoring or sacrificing the resolution of one set over the another. Another consideration is analysis time. Faster average linear velocities decrease analysis times. Sometimes a small amount of resolution is willingly sacrificed to obtain shorter analysis times.

Selecting the best average linear velocity is often an excercise in compromise. Sometimes a single carrier gas velocity is optimal for all of the sample compounds; this is often not the case. Maximum resolution often comes at the cost of longer analysis times. Finding the best balance or resolution for the various peaks and analysis times requires some forethought and experimentation.