Connections

Measuring Column Flow and Velocity

John Hinshaw discusses the measurement of column flow and its interrelationship with carrier-gas velocity in this month's "GC Connections."

Gas chromatographers should be concerned about column flow and velocity. Whether selecting a capillary column to meet specific separation requirements, setting up a column in an instrument, or attempting to diagnose a column problem, analysts need to know both the column velocity and flow. Working without these figures is like trying to drive a car at night with no speedometer and the headlights turned off; you won't know how fast you're going to get to the end of your journey, and you won't know what shape your automobile will be in when you arrive.

The column velocity — or more precisely the carrier-gas linear velocity through the column — tells chromatographers how quickly the chromatography will take place and how efficiently a column can resolve the peaks, given no external interference. Operating close to optimum velocity provides a compromise between speed of analysis and column efficiency. Running at high velocities produces a chromatogram more rapidly but sacrifices some column efficiency, which may be a desirable result in many cases. Low velocities take longer to deliver a relatively poor result and are rarely selected. Optimum velocity values depend upon the column characteristics, the sample, the temperature, and the carrier-gas type, but they generally are 20–60 cm/s.

The carrier-gas flow rate, on the other hand, tells chromatographers how well the column suits the hardware at its entrance and exit. If the column flow is too low or too high, the inlet might not deliver sample to the column without causing some peak distortion, loss of sample integrity, or other side effect. Some detectors — mass spectrometers, for example — tolerate flows as high as their maximum rate, above which the detector performance declines. Other detectors can require a minimum flow rate or some other considerations to function well. Low flow rates for capillary columns work well in a direct interface with a mass spectrometer, but such columns can require makeup gas with, for example, a flame ionization detector designed for packed columns. Conversely, a packed column won't work well when interfaced directly with a mass spectrometer — its flow is too high and a stream-splitting interface would be necessary — but the same column will be fine with a conventional flame ionization detector without makeup gas.

Chromatographers can use the linear velocity to determine how rapidly a column will deliver a chromatogram and how efficiently it should perform, and they can ascertain inlet–column–detector compatibility from the flow rate. Of course, they must consider the gas chromatography (GC) system as a whole to make meaningful choices about these two column variables because they depend upon each other as well as upon the column dimensions and operating conditions.

Column Dynamics

The dynamics of carrier-gas transport through GC columns can explain the measurement of capillary column linear velocities and flows. In a column chromatography system, higher pressure at the column inlet forces the mobile phase to flow through the column to the outlet and transport solute molecules across the stationary phase. Unlike in liquid chromatography (LC) columns, where the mobile phase is not compressible, the gaseous mobile phase is compressible in GC columns and systems. Carrier-gas compressibility in GC causes the velocities and flows at the beginning and end of the column to be different. Gas chromatographers need to take this factor into consideration to express the flow and velocity in a meaningful way that facilitates column evaluation and operating condition selection.

Figure 1 illustrates an open tubular (capillary) GC column, its dimensions, and

John V. Hinshaw
GC Connections Editor

some of the flow, pressure, and velocity measurements under discussion (1).

Volumetric flow gradient: When a carrier pressure drop is established across a GC column, gas begins to flow into the tube. After a moment, gas also starts to flow from the column exit. After all the air has been purged from the column and the flow has stabilized, the mass of carrier gas flowing into the column per unit time must be equal to the mass flow rate from the column exit, as long as no leaks occur along the way. Outside of a physical chemistry class and, for that matter, in the class too, it's inconvenient to collect carrier gas for a period of time and then weigh it, so chromatographers don't measure mass flow directly. Instead, we express mass flow in terms of a measured volumetric flow corrected to a standard temperature and pressure, usually 101 kPa (1 atm) and 25 °C, which are close to the ambient conditions in many laboratories. Expressing flows under standard conditions enables analysts to compare different columns easily.

The classical bubble flowmeter approximates the total volume of gas that passes through it in a given time period, from which the operator can calculate the volumetric flow rate in cubic centimeters per minute or other convenient units. Bubble flowmeters are prone to several errors, however, including low apparent flows because of diffusion of carrier gas through the soap bubble–gas interface and the presence of water vapor. The calculation of mass flows from bubble meter volumetric flows also requires knowledge of the room temperature and atmospheric pressure. Although every chromatographer should know how to use one, I don't recommend using bubble flowmeters for routine measurements. A digital flowmeter compensates for current ambient conditions and corrects the readout to standard conditions with little or no operator intervention beyond periodic factory recalibration.

The effects of carrier-gas compressibility on volumetric carrier-gas flows can be significant in certain situations. At high inlet pressures, the volumetric flow at the column inlet will be much less than that at the column exit. This difference in flow rates in turn can affect the operation of inlet splitters and related sampling devices.

Consider a 30 m × 100 μm high-speed column operating at 100 °C with enough helium pressure to generate a linear velocity of 30 cm/s. The required pressure drop (gauge inlet pressure) is 800 kPa (116 psig) at an absolute outlet pressure of 101 kPa (atmospheric pressure). At this level, the column mass flow is 0.68 cm^3/min (expressed at 25 °C and 101 kPa, see the "Velocity gradient" section below for the calculation). For a split ratio of 50:1, I would need a split flow rate of 34 mL/min, as corrected to the same ambient conditions as the column mass flow rate. However, if I consider that the carrier gas is compressed to 901 kPa absolute pressure in the inlet, and if I ignore minor effects caused by an elevated inlet temperature, the corresponding volumetric split flow at the inlet pressure actually is only 3.7 mL/min, and the corresponding volumetric column flow in the inlet is 95 μL/min.

The internal volume of a typical 4-mm i.d. split-inlet liner is approximately 1 mL, which implies that it will take about 30 s or more to clear 90% of the contents of the inlet liner into the column or out through the split vent after injection. This slow injection speed does not bode well for the very narrow peaks that gas chromatographers would expect from this column. Instead, I might choose a rapid temperature program that starts at temperatures cool enough to immobilize the inlet-broadened peaks immediately after they enter the column and to trap them in a narrow band for release along the column after the temperature program has commenced. This situation can be improved by using a splitter with a narrow 1–2 mm i.d. liner, which has the effect of transferring the sample into the column as much as 16-fold faster. These narrow liners impose a limit upon the injected sample volume of approximately 0.1–0.5 μL, depending upon the solvent, temperature, and liner, to avoid excessive vaporized sample volumes that can leave an inlet liner and flash into other inlet parts or even into the pneumatic supply system.

From this example, you can see that consideration of the differences in flow at the column inlet and exit can be critical both in choosing sensible operating conditions and in diagnosing an injection problem onto certain types of columns.

Velocity gradient: Gas chromatographers often speak of the carrier-gas linear velocity through a capillary column. This parameter is the speed in centimeters per second at which the carrier-gas molecules move along a column. The velocity is important in two ways: First, it provides a good measure of how efficiently a column is operating when compared with the optimum linear velocity as measured or calculated from theory. Sec-

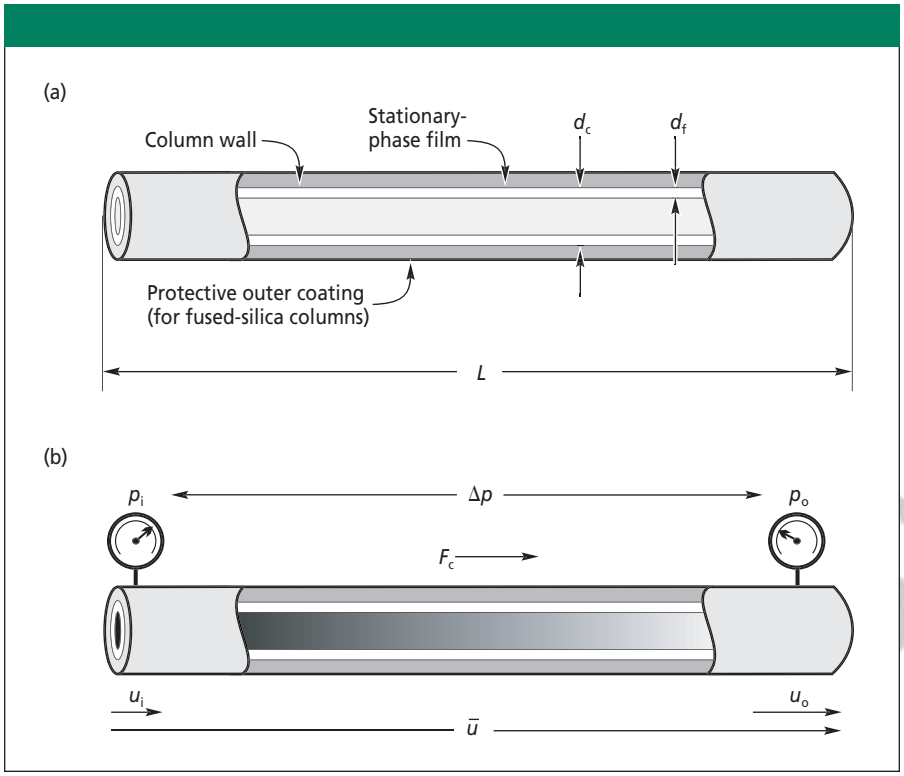

Figure 1: Schematics of open tubular columns that illustrate (a) column dimensions and (b) column pressures, flows, and carrier-gas linear velocities. Relative dimensions are exaggerated for emphasis (1).

ond, using the linear velocity to compute very low capillary column flow rates can be more accurate than using a bubble or electronic flowmeter, especially if analysts can't afford both a low- and a high-range device.

The carrier-gas linear velocity at the column exit (u_0 in Figure 1b) is higher than at the entrance (u_i in Figure 1b), because of the same gas-compression effects that produce lower volumetric flows at the column entrance. By necessity, gas chromatographers determine the *average* carrier-gas linear velocity, instead of the inlet or outlet velocities, by measuring the time that it takes a substance unretained by the stationary phase to transit the column length. This unretained peak time (t_M) divided into the column length (L) gives the average carrier-gas linear velocity ($\bar{u}$):

$$\bar{u} = \frac{L}{t_M} \qquad [1]$$

In this case the unretained peak time is 100 s, which indicates an average velocity of 30 cm/s.

With the inlet pressure (p_i) and outlet pressure (p_0), chromatographers can compute the outlet linear velocity with a compressibility correction factor (j):

$$j = 1.5\frac{\left(p_i/p_o\right)^2 - 1}{\left(p_i/p_o\right)^3 - 1} \qquad [2]$$

$$u_o = \frac{\bar{u}}{j} \qquad [3]$$

For the example of the high-speed column in the previous section, the inlet gauge pressure was 800 kPa and the outlet pressure (p_0) can be assumed to be 101 kPa, so that p_i is 901 kPa. This calculation gives a j factor of 0.1662, so if the average carrier-gas linear velocity is 30 cm/s, then the outlet velocity is 180 cm/s. The inlet and outlet velocities are related by the relative pressure ($P = p_i/p_0 = 8.95$), so the inlet velocity would be 20 cm/s. The average linear velocity is not equal to the average of the inlet and outlet velocities, because the velocity increases in a nonlinear fashion along the column length.

Now, how do I use this information to calculate the volumetric column flow rate? If I know the speed at which the carrier gas exits the column, then I can multiply this value by the cross-sectional area (A) of the column ($A = \pi d_c^2/4$) to determine the volumetric flow rate at the column exit (F_c):

$$F_c = A\,u_o = \frac{\pi\, d_c^2\, \bar{u}}{4j} \qquad [4]$$

where d_c is the column diameter.

For a column diameter of 100 µm (0.01 cm) and an average velocity of 30 cm/s at j factor value of 0.1662, I obtain an outlet flow of 0.85 cm^3/min (did you remember to multiply the result by 60 to convert from mL/s to mL/min)? This flow is the volumetric column flow at the column operating temperature of 100 °C. To convert to the mass flow corrected to 25 °C (F_a), I must multiply the volumetric flow by the ratio of the reference temperature (T_a) to the column temperature (T_c), both in Kelvin:

$$F_a = F_c\left(\frac{T_a}{T_c}\right) \qquad [5]$$

The result yields an F_a of 0.68 cm^3/min. Table I summarizes these column parameters, both measured and calculated.

One mistake that many gas chromatographers make is to calculate the column flow rate from the average carrier-gas linear velocity without compensating for carrier-gas compressibility by omitting the j factor and without adjusting the flow rate to a standard reference temperature such as 25 °C. Leaving out these corrections makes it difficult, if not impossible, to compare results from multiple instruments and columns. The omissions also can lead to the misdiagnosis of a GC problem related to flow or velocity settings.

Table I: Summary of measured and calculated column parameters

Parameter	Symbol	Value
Measured		
Column length	L	30 m
Column inner diameter	d_c	100 µm (0.01 cm)
Inlet pressure	p_i	800 kPa
Outlet pressure	p_0	101 kPa
Column temperature	T_c	100 °C
Unretained peak time	t_M	100 s
Calculated		
Average carrier-gas linear velocity	$\bar{u}$	30 cm/s
Relative pressure	P	8.92
Compressibility correction factor	j	0.1662
Outlet carrier-gas velocity	u_0	180 cm/s
Inlet carrier-gas velocity	u_i	20 cm/s
Column outlet volumetric flow rate (at 100 °C)	F_c	0.85 cm^3/min
Column inlet volumetric flow rate (at 100 °C)	F_i	0.095 cm^3/min
Column mass flow rate (at 25 °C and 101 kPa)	F_a	0.68 cm^3/min

Conclusion

The column flow rate and the carrier-gas linear velocity play important roles in determining column efficiency and in judging how well a column functions with system inlets and detectors. The flow and the velocity are different at the column inlet and outlet because of carrier-gas compressibility. Gas chromatographers can compensate for the effects that expanding carrier gases create as they move down the column. By adjusting the calculations to express these values under a standard set of reference conditions, analysts can compare results from different columns and instruments under different conditions more easily. Using the measured average carrier-gas linear velocity to determine low capillary column mass flow rates can be more accurate than attempting to use a flowmeter — bubble or digital — that is designed for higher flow rates.

Reference

(1) J.V. Hinshaw and L.S. Ettre, *Introduction to Open-Tubular Column Gas Chromatography* (Advanstar Communications, Cleveland, Ohio, USA, 1994), p. 16.