Making Sense of GC

Flow Calculations - Part 1

Customers have often asked about the difference in measured flow rate to theoretical flow rate based on nominal column diameters and lengths. This article attempts to demystify the theoretical flow formula and explain the significance of various parameters used. A summary of the outcomes of changing column dimensions and carrier gas is summarised below.

- **changing the column internal diameter by 2% will change the column flow rate by 8%**
- **cutting 5 metres off a 30 metre column will increase the flow rate by 17%**
- **changing from helium to hydrogen will more than double the flow rate**

The flow rate equation begins with the standard Poiseuille Flow calculations for incompressible fluids and is modified to take into account compressible gases (see insert). This short article is Part 1 of a two part series. By providing examples, the importance of various factors such as column internal diameter and length will be explained. Part 2 of this series will consider carrier gas velocity.

Calculating flow rate using the modified Poiseuille equation

GC users are increasingly using software programs to calculate flow rate. Values obtained are sometimes compared with measured flow rates obtained by a bubble meter so we decided to compare the two. **Equation 2** is a modification of Equation 1 and allows the use of everyday units such as psi for pressure, meters for length and Celsius for temperature.

The length and diameter of a well-used BPX5 column were measured and found to be 27.55 metres and 0.245 mm ID, respectively. The column length was measured by counting the number of coils and using **Equation 3**. The internal diameter was measured using a light microscope. This column had begun life with a nominal length of 30.0 metres but several cuts had reduced this to 27.55 metres. The nominal diameter of the column was 0.250 mm. The inlet pressure was set at 20 psi and the viscosity of helium was calculated as 208 micropoise using the **Helium Viscosity Equation** *(refer opposite page)*. The flow was measured at atmospheric pressure and 25°C. An oven temperature of 50°C was set.

The measured flow rate using the bubble meter was 2.03 mL / min is close to the calculated flowrate of 1.98mL/min using the modified Poiseuille equation.

$$50{,}747 \cdot \frac{0.245^4}{208 \text{ x } 27.55} \cdot \frac{\{(20 + 14.7)^2 - (0 + 14.7)^2\}}{14.7} \cdot \frac{14.7}{14.7} \cdot \frac{(25 + 273)}{(50 + 273)} = 1.98\text{mL} / \text{min}$$

It is important to remember that this is the flow rate at the column outlet. To optimize chromatography, one is really interested in the average linear carrier gas velocity and the inlet pressure needed to obtain this value for a column of certain dimensions. This discussion will be continued in part 2.

The effect of internal diameter and length on column flow rate

It can be clearly seen from an examination of Equation 1 that volumetric flow is directly proportional to the fourth power of the radius (diameter / 2). Thus a small change in internal diameter can make a significant difference in calculated flow. For example, a deviation of only 5 microns in a column of internal diameter of 250 microns (a 2% change) will change the flow by 8%.

Table 1. Data showing calculated flows (mL/min) of helium at various internal diameters and lengths. An inlet pressure of 10 psi was used in the modified Poiseuille Equation 1.

Column ID (mm)	Column Length (metres)		
	25	30	35
0.245	0.69 mL/min	0.57 mL/min	0.49 mL/min
0.250	0.75 mL/min	0.62 mL/min	0.53 mL/min
0.255	0.81 mL/min	0.67 mL/min	0.58 mL/min

Gas viscosity is taken as 228.1 micropoise at 100°C (reference CRC Handbook of Chemistry and Physics 59th edition)

Mathematically, it appears from Equation 2 that column flow rate is inversely proportional to column length. This is true provided that the inlet to outlet pressure differential remains constant. In a practical sense though, it is true because as the length increases so does the restriction and therefore the pressure must rise to maintain the same flow rate.

If we examine the data in **Table 1**, decreasing the column length from 30 to 25 metres will increase the flow rate from 0.62 to 0.75 mL/min. Column length can be calculated by counting the number of turns and using Equation 3. For example, for a 17.5 cm cage, a 25 metre column should be 45.5 turns or 55 cm per turn.

Equation 3: $$\text{Length} = (\text{no of turns}) \cdot \pi \cdot (\text{diameter of column in cage})$$

At SGE, we understand the importance of tight tolerances for internal diameter and length and we have precise control over these parameters because all fused silica tubing used for our capillary columns is manufactured in-house.

The effect of temperature and pressure

A close examination of the modified Poiseuille equation shows that the pressure and temperature of both the outlet and the column are critical. Column temperature will affect gas viscosity and because gases become more viscous as they are heated, the flow rate will decrease as the viscosity and temperature increase.

The temperature of the outlet is also critical. Using **Equation 2**, for a 30m x 0.25mm ID column, a measured (outlet) temperature of 25°C and an oven temperature of 200°C will give a theoretical flow rate of 1.05 mL/min. This will be close to the value of the measured flow rate at this temperature as demonstrated above. However, if the actual measured (outlet) temperature is 200°C, the theoretical flow rate will now be 1.66 mL/min. This is a more realistic flow rate of the carrier gas as it passes through a hot detector and a measurement of flow rate with a bubble meter will give a misleading result.

The following **Viscosity Equations** may be used to calculate the viscosity of the carrier gas at any temperature from 0 to 300°C.

For **Nitrogen** Viscosity $(\eta) = 15.43 \cdot \sqrt{t_c + 273} - 89.4$ μpoise (correcct to within ± 0.5%)

For **Hydrogen** Viscosity $(\eta) = 7.42 \cdot \sqrt{t_c + 273} - 39.5$ μpoise (correcct to within ± 1%)

For **Helium** Viscosity $(\eta) = 16.5 \cdot \sqrt{t_c + 273} - 87.8$ μpoise (correcct to within ± 0.8%)

A modification of Poiseuilles Formula

Equation 1

$$V_o = \frac{3.75\pi r^4}{\eta 1} \cdot \frac{\{p_i^2 - p_o^2\}}{p_o} \cdot \frac{p_o}{p_m} \cdot \frac{T_m}{T_o}$$

The formula above, for the flow per minute, was the derived from first principles, and is correct provided a consistent set of units is used. The formula below is a modification to allow the use of more practical units in everyday use.

Equation 2

$$V_o = 50{,}747 \frac{d^4}{\eta 1} \cdot \frac{\{(p_i^2 + 14.7)^2 - (p_o + 14.7)^2\}}{(p_o + 14.7)} \cdot \frac{p_o}{p_m} \cdot \frac{(T_m + 273)}{(T_c + 273)}$$

where:

V_o	is the carrier gas volume flow rate in mL per minute
d	is the internal diameter of the capillary column (including the internal coating) in mm
η	is the dynamic viscosity of the carrier gas at the operating temperature, in micropoises
1	is the length of the capillary column in metres
p	is the carrier gas inlet pressure in psi (above atmospheric)
p_o	is the carrier gas outlet pressure in psi
p_m	is the pressure at which the measurement is made
t_c	is the temperature of the column in °C
t_{rr}	is the temperature at which the measurement is made (outlet temperature)

Making Sense of GC

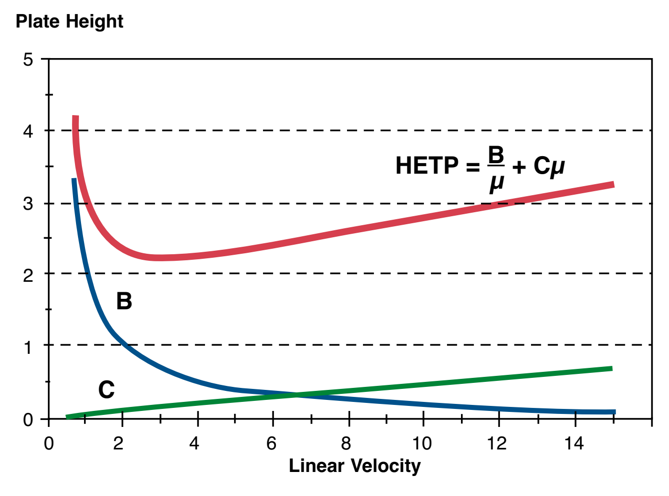
Flow Calculations - Part 2

IMPORTANT INFORMATION. The inner diameter can vary from 0.245 to 0.255 mm for a typical 0.25 mm ID column. Therefore, when the inlet pressure and length are held constant, the flow rate can change by 16%. This stresses the importance of measuring and optimizing the linear carrier gas velocity after installing a new column.

Why measure or calculate the flow rate?

Flow rate is an important parameter in gas chromatography because it directly effects split ratio in a split injection. Split ratio is the ratio of the flow rate of gas through the split vent to the flow rate through the column. For example, if the flow rate of gas through the split vent is measured at 100 mL/minute column and the flow rate is 1.0 mL/minute, then the split ratio is 100:1. Correction can be made for measurement at different pressure and temperatures for precise calculations.

Figure 1. Van Deemter Curve



Why measure average linear velocity?

The average velocity is a function of the time it takes for a carrier molecule to get from one end of the column to the other. At the start of the column, molecules will move slowly (because of the high back pressure) but will speed up as they approach the end of the column (towards lower back pressure). The measured gas velocity is their average speed in the column. So why is this important to the chromatographer?

The reason is that there is an optimum value for the average carrier gas velocity to achieve maximum efficiency. By maximizing efficiency, resolution is also maximized. If the column dimensions change, gas velocity may stray from the optimum. The optimum value will depend on the nature of the carrier gas, column diameter, column length, film thickness and other variables. The linear carrier gas velocity can be easily measured (see box below).

Why is there an optimum value for the carrier gas velocity?

The molecules of your sample will enter and exit the stationary phase (partition) and will spend a different amount of time in the phase compared to different sample molecules. There is an ideal time for the sample molecules to spend inside the column and this is determined by the average gas velocity (μ). If the molecules spend too much time in the column, they will broaden (peak broadening) and diffuse into different sample molecules and might not be separated at the end. If the molecules don't spend enough time inside the column, they won't interact with the stationary phase long enough to achieve a separation.

These two factors are described by the B and C terms of the Van Deemter equation, respectively. The Van Deemter curve is shown in **Figure 1.** The lower the HETP (height equivalent of a theoretical plate), the better the column performance.

The average carrier gas velocity is the important parameter and should be set in the optimum range (see box below) after column installation.

Equation: Measure your carrier gas velocity

$$\text{Carrier gas velocity (cm/sec)} = \frac{\text{Length of column (cm)}}{\text{hold-up time in seconds of a non-retained solute } (t_m)}$$

Optimum ranges for carrier gas velocities:

Hydrogen = 30 – 50 cm / sec
Helium = 20 – 40 cm /sec
Nitrogen = 10 – 15 cm / sec

The hold-up time is measured from the retention time of an unretained component (such as methane) in the column.