Chromatography Solutions

Knowledge note #0010

Chromatographic band broadening and the van Deemter equation

INTRODUCTION

In liquid chromatography, several processes contribute to the broadening of analyte bands (or peaks) which may result in loss of resolution and method performance. Whilst some degree of band broadening is unavoidable, an understanding of the underlying processes is useful to attempt to minimise their impact. The van Deemter equation[1] is one of the fundamental concepts in chromatography and a useful expression which describes elements of band broadening and column efficiency.

BAND BROADENING

Band broadening encompasses any process that results in the spreading of an analyte band as it migrates through the LC system and column. In practical terms, band broadening (i.e. an increase in peak width) results in loss of efficiency, loss of resolution and deterioration of the chromatographic performance of a method.
The van Deemter equation, derived by J. J. van Deemter, describes the various factors which contribute to band broadening. The work derived a composite curve to relate the column efficiency (expressed as Height Equivalent to a Theoretical Plate, *HETP*) to the linear velocity of the mobile phase as it flows through the column. Although derived from the theory of gas chromatography, the model has been found to be equally applicable to liquid chromatography.
Whilst detailed knowledge of the equation is often not necessary, a broad understanding of the concepts involved provides the chromatographer with useful insights into factors influencing the performance and optimisation of analytical methods.

THEORETICAL PLATES

The efficiency of a column is often referred to in terms of the number of theoretical plates, or plate count, *N*. A theoretical plate is a hypothetical boundary between two phases (e.g. solid and liquid) which are in equilibrium. A chromatographic separation relies on having a series of such plates and the more plates, the higher the efficiency. For the purposes of this discussion, the column can essentially be considered as being divided into a stack of discs, or plates. The higher the number of plates,

the higher the column efficiency. *N* is proportional to retention time and inversely proportional to peak width. For a column of length *L*, we can define the height of each plate by dividing the column length by the number of plates. This value is commonly referred to as the height equivalent to a theoretical plate.

$$HETP = L/N \qquad \text{Equation 1}$$

THE VAN DEEMTER EQUATION

In its simplified form (equation 2), the van Deemter equation describes three terms which contribute to band broadening inside an LC column (*A*, *B* and *C*) and relates them to the mobile phase linear velocity (*u*).

$$HETP = A + B/u + Cu \qquad \text{Equation 2}$$

The three terms correspond to the following processes:

A Eddy diffusion,

B Longitudinal diffusion,

C Mass transfer.

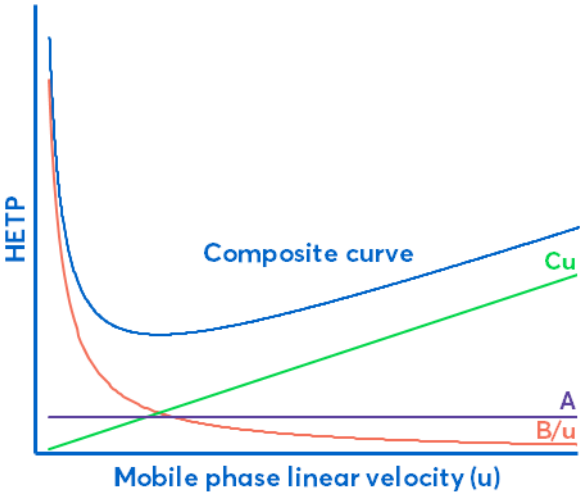

Figure 1: van Deemter curve

Plotting *HETP* against the mobile phase linear velocity (i.e. flow rate) generates the composite plot shown in Figure 1. By considering this plot, it is possible to understand the influence of each of the three terms on column efficiency.

A: Eddy Diffusion

An analyte molecule in a chromatographic band may take any one of many different paths through the column packed bed, which leads to a general broadening of the peak as it passes through the column. The *A* term can be reduced by using well packed columns and using smaller particle sizes with a narrow particle size distribution.

B: Longitudinal Diffusion

Within an analyte band, analyte concentration is greatest at the centre. Therefore a concentration gradient exists and as the band migrates through the column, analyte molecules tend to disperse outwardly from the peak centre, causing the band to broaden.

Figure 1 shows that longitudinal diffusion reduces at higher linear velocities and can therefore be reduced by operating at a higher flow rate. Importantly, longitudinal diffusion will also occur within any system dead volume. It is therefore important to minimise connecting tubing where possible and ensure that it is correctly installed with good fittings.

C: Mass Transfer

In LC, the stationary phase is typically a porous silica based material. At a microscopic level, pores at the silica surface can be considered to be filled with non-moving or stagnant mobile phase. Analyte molecules may penetrate the pores and migrate to the stationary phase surface by diffusion only and will have different residence times according to how deeply they enter the pores (denoted as 1, 2 and 3 in Figure 2). The effect of this process is a broadening of the analyte band. From Figure 1, the mass transfer term is more dominant at higher flow rates. Mass transfer can be reduced by using a smaller particle size or by heating the column to increase the rate of diffusion.

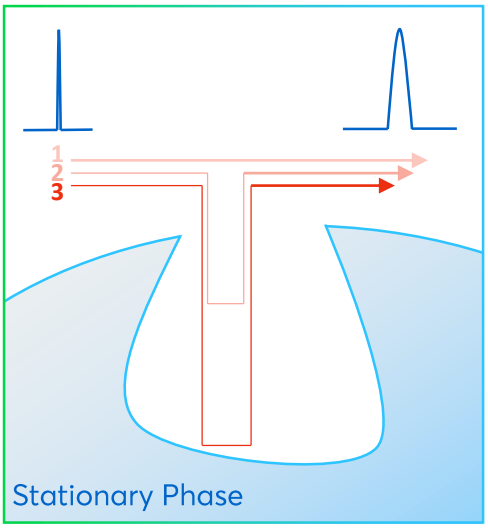

Figure 2: Schematic representation of mass transfer.

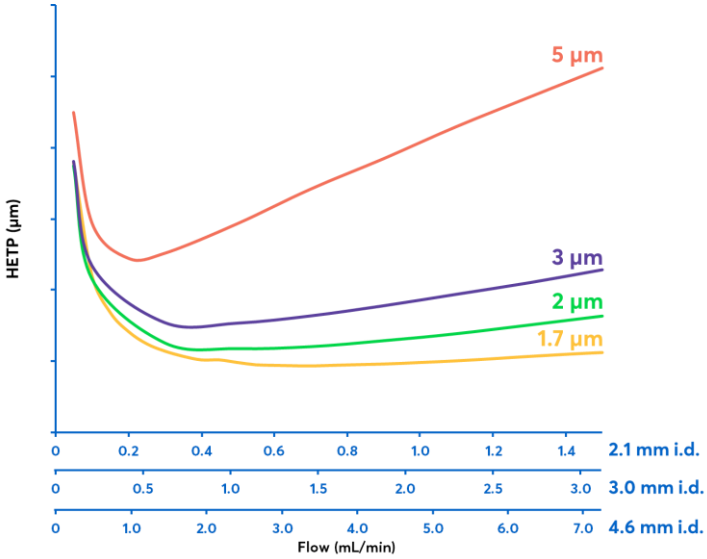

Figure 3: Van Deemter plots for Avantor® ACE® columns packed with different sized particles.

What Does This Mean Practically?

In practical terms, the maximum column efficiency can be achieved at a specific linear velocity or flow rate, at the minimum of the curve in Figure 1. It is therefore essential to set a suitable flow rate to minimise the *B* and *C* terms. Operating at too high or low a flow rate will result in a loss in efficiency. In order to minimise the *A* term, it is important to use well packed columns containing high quality packing materials, such as the Avantor® ACE® range. The *B* term can also be reduced by ensuring that system tubing is kept as short as possible.

The van Deemter curve is also useful when comparing particle sizes. As shown in Figure 3, the smaller the particle size, the more efficient the column (i.e. lower HETP). In addition, it is apparent that for smaller particles, the optimum flow rate is higher than for larger particles. It is therefore important to work at elevated flow rates to achieve the full potential performance of smaller particles. Additionally, the curve is flatter at higher flow rates for sub-2 micron particles, which means that even higher flow rates can be utilised to achieve ultra-fast UHPLC separations.

CONCLUSION

The van Deemter equation and its constituent terms provide a useful insight into band broadening processes. This should enable chromatographers to understand potential instrument and column effects on the efficiency of separations.

[1] J. J. Van Deemter, F. J. Zuiderweg, A. Klinkenberg, (1956), Chem. Eng. Sc. 5 271-289