

Active Flow Technology – Understanding How the Flow Rate Profile Affects the Chromatographic Efficiency

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Overview

The use of active flow technology is presented, demonstrating the benefits for the chromatographic efficiency of removing the peripheral flow and analyzing just the flow from the central region of the column. Using a model developed by Gritti [1], a comparison between a simulation with and without radial mass transfer effects included is compared to experimentally derived data.

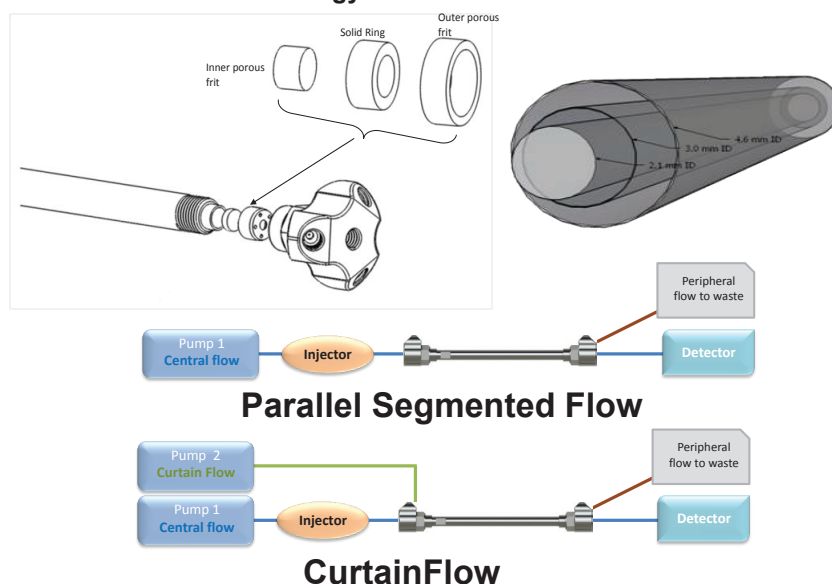
Introduction

Active Flow Technology (AFT) is the term that encompasses a range of new chromatography columns that are designed to eliminate wall effects, minimise solute band broadening due to radial heterogeneity and decrease the peak volume of eluting components. This is achieved through the use of novel endfittings which separate the peripheral flow from the central flow. These endfittings have been used in two different configurations, namely with the endfitting solely at the outlet of the column, referred to as parallel segmented flow (PSF), or with the endfitting placed at both the outlet and the inlet of the column, referred to as curtain flow (CF). Figure 1 shows a diagram of the endfitting and the two possible configurations.

Studies detailing the practical gains in separation performance of AFT columns have been published [2,3] on particle packed column formats from the preparative scale down to narrow bore columns. These formats of columns have also been demonstrated on monolithic columns. The results have shown conclusively that substantial gains in efficiency are obtained, although the gains cannot be generalised as they are dependent on numerous factors, which include column length, flow rate, particle diameter, the degree of retention and the segmentation ratio. Nevertheless, the magnitude of the gain in chromatographic performance is typified by the results reported on analytical scale columns packed with reversed phase silica particles, which were in the order of 20% in efficiency (N) in comparison to conventional columns of the same internal diameter.

This poster will investigate if the improvements in efficiency can be effectively modelled, to better understand how the retention of analytes is affected by splitting the peripheral flow from the central flow. Experimental data will be compared with modelling data to demonstrate the applicability of the modelling work. Initially, only the parallel segmented flow will be considered.

FIGURE 1. Design of the endfitting and the two configurations under evaluation for the Active Flow Technology



Experimental

Performance of Parallel Segmented Flow

Columns: Thermo Scientific™ Hypersil GOLD™ 5 μm , 100 x 4.6 mm

(in standard and PSF configurations)

Mobile phase: 70:30 methanol:water

Segmentation ratio at column outlet: 10 to 65% every 5%;

Injection volume: 5 μL

Test solutes: Theophylline, propylbenzene.

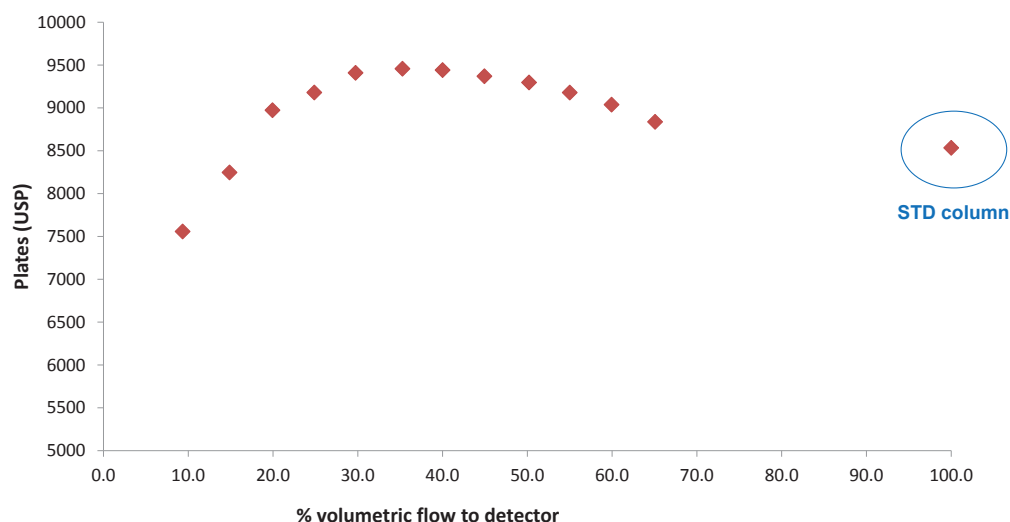
The frit had an internal surface area to peripheral surface area ratio of 1:6, which would result in a natural split ratio of, assuming no load post column, of 5 parts going to the peripheral flow (waste) and 1 part going to the detector. A series of experiments were initially performed to identify the optimum split ratio using this configuration of frit. This was achieved by varying the post column load on the peripheral line by using different lengths of tubing and therefore pressure applied to column outlet. Monitoring the flow to the peripheral line allowed a determination of the correct flow rate ratio, and hence allowed the size of the virtual column within the physical column to be determined.

Initially the standard column configuration was tested, and this was then followed by testing of the parallel segmented flow outlet. van Deemter plots were plotted for both configurations, obtained by monitoring the chromatographic efficiency vs. the flow rate.

Results

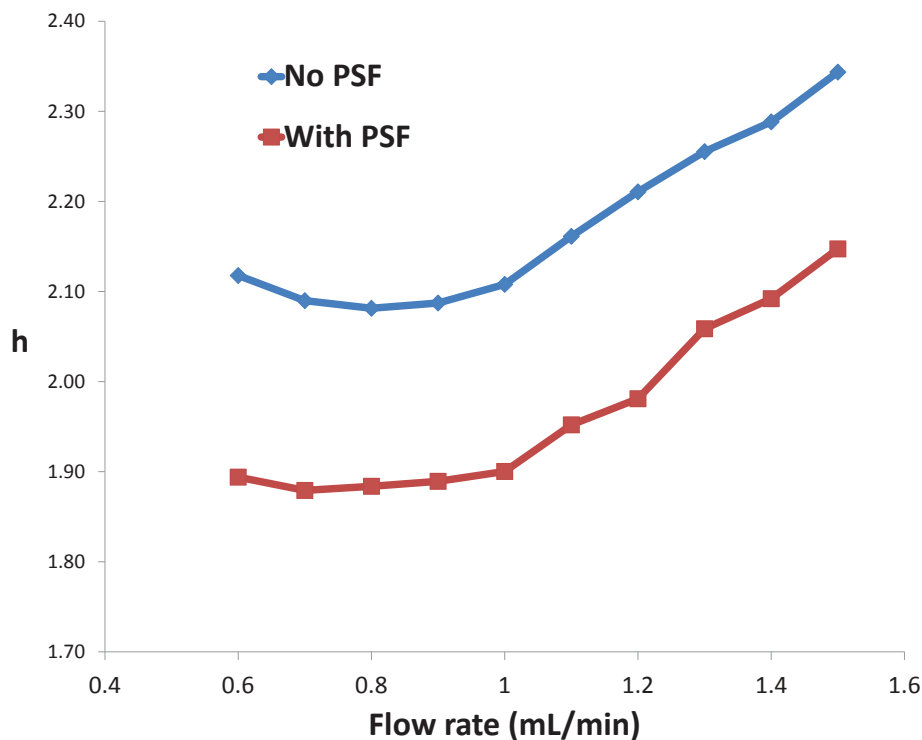
The data obtained for these first set of experiments is shown in Figure 2. This diagram shows that as the flow to the detector is decreased from 100 to 40%, effectively decreasing the size of the virtual column, the chromatographic performance increases. A maximum is reached at about 30–40%. However, it is thought that this observed reduction in performance at very low flow rates to detector (virtual diameters) may be due to the band dispersion post column in the connecting tubing and in the detector. This hypothesis has not yet been tested though.

FIGURE 2. Effect of varying the flow to the detector, effectively altering the diameter of the virtual column



The van Deemter plot shown in Figure 3 clearly shows that there is an improvement in chromatographic performance of about 10–20% when using the AFT. The data obtained in these experiments also shows consistency across the flow rate range, and that there does not appear to be a flow dependency on the improvement observed under the conditions used in this experiment.

FIGURE 3. van Deemter plots with and without the parallel segmented flow technology



Modelling

There are a variety of dispersion models available for modeling of dispersion processes in a chromatographic system. A very comprehensive review of these models was given by Gritti [1] who suggested the following model to simulate the dispersion processes in a column. One advantage of this model is that there is a radial dispersion term incorporated which allows for a very simple evaluation of parallel segmented flow technology. There are three terms typically used to describe the dispersion processes within a packed bed, referred to as A (eddy dispersion), B (longitudinal dispersion), and C (resistance to mass transfer).

A term

The A term has been the topic of much conversation in academic journals. Initially this was considered flow independent, but work by Knox [4] and many others demonstrated that there is a flow dependency associated with this term. Other work has demonstrated that the term can be decoupled and considered as a combination of short range dispersive effects and also long range trans column effects, due to the effects of the wall. This is ideal for modeling the AFT, as the radial dispersion of the packing material can either be added to the model or removed as required (Equation 1). All the terms are explained in Figure 4.

Equation 1. Model used for the A term incorporating a trans column dispersion term

$$H_{Eddy,TC,diffusion} = \frac{d_p}{\frac{p_2}{2p_1 m_l \omega_{\beta,c}^{*2}} + \frac{\epsilon_t (D_{eff} + 0.5 \epsilon_s \gamma_r D_m v) (1 + k)}{\epsilon_s C_m m_r^2 D_m v}}$$

B Term

The Torquato model has been used to describe the longitudinal dispersion process as a function of flow rate. This model has been successfully used to describe beds packed with fully porous media as well as solid core material. One area that has been investigated is the use of solid core material and it is envisaged that using a more general equation will allow for the model to be more applicable to different types of substrate designs. The equations which describe this are given in equation 2.

Equation 2. Torquato model used for the B dispersion term

$$D_{eff} = \frac{1}{\epsilon_s (1 + k_1)} \left[\frac{1 + 2(1 - \epsilon_s)\beta - 2\epsilon_s \xi_2 \beta^2}{1 - (1 - \epsilon_s)\beta - 2\epsilon_s \xi_2 \beta^2} \right] D_m$$

$$\beta = \frac{\frac{1 - \rho^3}{1 + \frac{\rho^3}{2}} \Omega - 1}{\frac{1 - \rho^3}{1 + \frac{\rho^3}{2}} \Omega + 2}$$

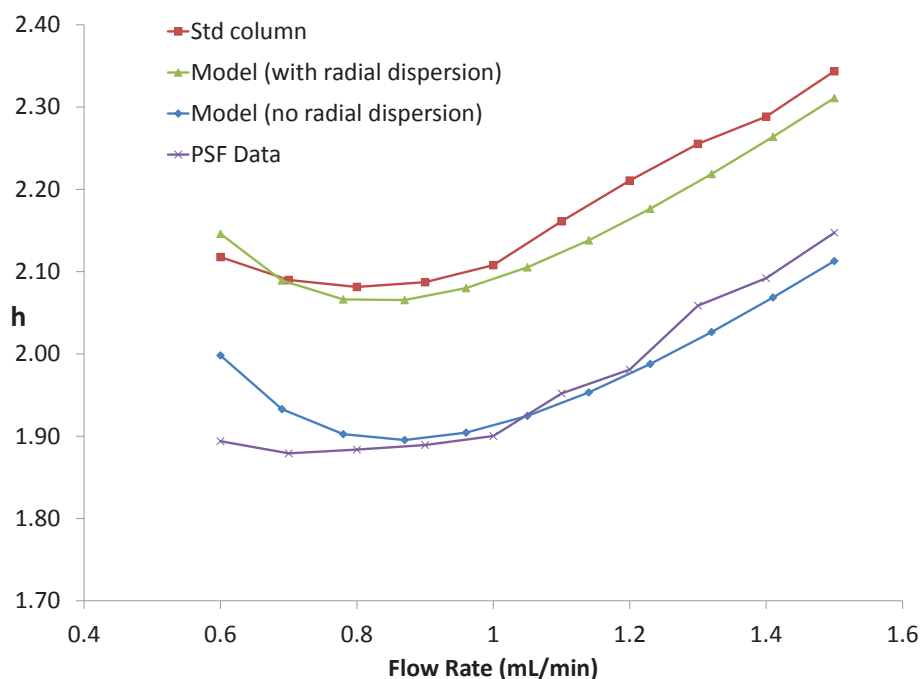
C Term

As with the A term there has been much discussion on the exact nature of the dispersion due to mass transfer. The C term does have flow dependency. It was noted during the modeling work, and using the parameters that relate to the practical component, that the C term did not contribute significantly to the band broadening. Therefore, for the initial work this term has been dropped, to allow simplification of the modeling processes.

The parameters used in the modeling are:

D_p (particle diameter) = 0.005mm, ϵ_t = 0.65 (total porosity of column), ϵ_e = 0.4 (external porosity of media in column), D_{eff} = 0.00051mm²s⁻¹, (effective diffusion coefficient), γ_r (factor for radial dispersion through convection)= 0.3, p_1 (integer derived from flow profile)= 8, p_2 (integer derived from flow profile)= 225, D_c (column diameter) = 4.6mm, D_m (bulk diffusion coefficient) = 0.001 mm² s⁻¹, k = 3.3 (capacity factor), m_r (ratio of column diameter to particle diameter)= 1700, Ω = 1, ξ (Torquato model parameter) = 0.328, ω_{bc} (the relative flow velocity between the centre and the wall of the column)= 1.5%

FIGURE 4. Comparison of experimental and modeling work



The data shown in Figure 4, shows that the model accurately matches the experimental data, given the same input parameters. The model also allows for the improvement in the chromatographic performance to be calculated when using solid core materials.

Conclusion

A model has been presented which simulates the dispersion processes that occurs in segmented flow and standard columns, by assuming that the trans (radial) column dispersion is either not present or is present. The model needs to be tested for robustness but initial data would suggest that it accurately reflects the experimentally derived data.

References

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