



# Occurrence of turbulent flow conditions in supercritical fluid chromatography



Ruben De Pauw<sup>a</sup>, Konstantin Choikhet<sup>b</sup>, Gert Desmet<sup>a</sup>, Ken Broeckhoven<sup>a,\*</sup>

<sup>a</sup> Vrije Universiteit Brussel, Department of Chemical Engineering (CHIS-IR), Pleinlaan 2, 1050 Brussels, Belgium

<sup>b</sup> Agilent Technologies Europe, Hewlett-Packard-Strasse 8, 76337 Waldbronn, Germany

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## ABSTRACT

Having similar densities as liquids but with viscosities up to 20 times lower (higher diffusion coefficients), supercritical CO<sub>2</sub> is the ideal (co-)solvent for fast and/or highly efficient separations without mass-transfer limitations or excessive column pressure drops. Whereas in liquid chromatography the flow remains laminar in both the packed bed and tubing, except in extreme cases (e.g. in a 75 μm tubing, pure acetonitrile at 5 ml/min), a supercritical fluid can experience a transition from laminar to turbulent flow in more typical operation modes. Due to the significant lower viscosity, this transition for example already occurs at 1.3 ml/min for neat CO<sub>2</sub> when using connection tubing with an ID of 127 μm. By calculating the Darcy friction factor, which can be plotted versus the Reynolds number in a so-called Moody chart, typically used in fluid dynamics, higher values are found for stainless steel than PEEK tubing, in agreement with their expected higher surface roughness. As a result turbulent effects are more pronounced when using stainless steel tubing. The higher than expected extra-column pressure drop limits the kinetic performance of supercritical fluid chromatography and complicates the optimization of tubing ID, which is based on a trade-off between extra-column band broadening and pressure drop. One of the most important practical consequences is the non-linear increase in extra-column pressure drop over the tubing downstream of the column which leads to an unexpected increase in average column pressure and mobile phase density, and thus decrease in retention. For close eluting components with a significantly different dependence of retention on density, the selectivity can significantly be affected by this increase in average pressure. In addition, the occurrence of turbulent flow is also observed in the detector cell and connection tubing. This results in a noise-increase by a factor of four when going from laminar to turbulent flow (e.g. going from 0.5 to 2.5 ml/min for neat CO<sub>2</sub>).

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## 1. Introduction

Having similar densities as liquids but with viscosities up to 20 times lower (lower diffusion coefficients), supercritical CO<sub>2</sub> may be the ideal (co-)solvent for fast and/or highly efficient separations without mass-transfer limitations or excessive column pressure drops. The lower diffusion coefficient results in a flatter C-term of the van Deemter curve in SFC, meaning that higher flow rates/velocities can be used with no significant performance loss [1]. However, the compressibility of a supercritical fluid makes it more difficult to accurately control the flow rates in a supercritical fluid chromatography (SFC) system and increases the difficulty of modeling such a system compared to liquid chromatography

[2]. The combination of a very low viscosity mobile phase with high velocities in the connection tubing, however, enhances the transition from laminar toward turbulent flow conditions, which have implications on average column pressure as well as operating pressure. T. A. Berger measured very low system dispersion values and pointed out turbulent effects in tubing and connections as the most probable cause, since these flow conditions lead toward a less pronounced radial velocity profile [3].

The pressure drop of a fluid flowing through any form of open tube is related to the average velocity of the fluid flow by the Darcy–Weisbach equation [4]

$$\Delta P = f_D \cdot \frac{L}{D} \cdot \frac{\rho_{av} \cdot u_{av}^2}{2} \quad (1)$$

where  $f_D$  is the Darcy friction factor,  $L$  the length of the pipe,  $D$  the hydraulic diameter (in case of a circular pipe, this is equal to the internal diameter,  $d_{tub}$ ),  $\rho_{av}$  and  $u_{av}$  are the average density and velocity of the fluid in the tube. In typical conditions encountered in

\* Corresponding author. Tel.: +32 26293781; fax: +32 26293248.  
E-mail address: [kbroekkh@vub.ac.be](mailto:kbroekkh@vub.ac.be) (K. Broeckhoven).

liquid chromatography, the fluid flow occurs under laminar conditions and when assuming the liquid is incompressible and exhibits Newtonian behavior, Hagen–Poiseuille showed that the value of  $f_D$  was given by

$$f_D = \frac{64}{Re} \quad (2)$$

where  $Re$  is the Reynolds number that is defined as the ratio of inertial forces to viscous forces and is calculated by

$$Re = \frac{\rho \cdot u \cdot D}{\mu} \quad (3)$$

With  $\mu$  is the dynamic viscosity of the fluid. Combining Eqs. (1)–(3), Poiseuille's law for the pressure drop in a circular tube ( $D = d_{tub}$ ) under laminar conditions is found

$$\Delta P = 32 \cdot \frac{L \cdot u \cdot \mu}{d_{tub}^2} = 128 \cdot \frac{L \cdot F \cdot \mu}{\pi d_{tub}^4} \quad (4)$$

With  $F$  is the mobile phase flow rate. In a practical liquid chromatography set-up, the flow rates are typically limited to 5 ml/min in combination with around 120  $\mu\text{m}$  as the narrowest tubing, using a mobile phase with a viscosity around 1 cP (1 mPa·s) and a density around 1000 kg/m<sup>3</sup>. Under these conditions, the mobile phase velocity in the tube is 7.4 m/s, corresponding to a  $Re$  of almost 900. As the transition from laminar to turbulent flow only occurs for  $Re$  numbers between 2300 and 4000, analytical liquid chromatography systems are generally used under laminar conditions. Only when e.g. tubing with an inner diameter of 75  $\mu\text{m}$  in combination with low viscosity solvents (e.g. pure acetonitrile or at elevated temperatures) with a viscosity around 0.4 cP, turbulent flow can occur ( $Re = 3500$ ). However, due to the excessive pressure drops (4th power dependency on  $d_{tub}$  for a fixed flow rate), this is seldom encountered in practice. In the case of supercritical fluid chromatography (SFC), with a very low viscosity of the mobile phase (10–20 times lower), the conditions for turbulent flow are reached more easily. Taking the same example as before ( $F = 5$  ml/min,  $d_{tub} = 120$   $\mu\text{m}$ ), but now for neat supercritical CO<sub>2</sub> ( $\mu = 0.07$  cP,  $\rho = 800$  kg/m), a  $Re$  number of a little more than 10,000 is found, showing that turbulent conditions can be expected from flow rates as low as 1.2 ml/min ( $Re$  equal to 2400) and certainly for flow rates above 2 ml/min. Optimal flow rates in SFC for 4.6 mm ID columns and 5  $\mu\text{m}$  are typically around 3–5 ml/min and for 2.1 and 3 mm columns packed with 1.8  $\mu\text{m}$  particles these can be expected to be in the range of 1–3 ml/min [1,5–7].

For supercritical fluids, where the flow rate ( $F$  (ml/min)) and thus the velocity increases with decreasing pressure along the column, it is easier to express  $Re$  as a function of the mass flow rate ( $\dot{m}$  (g/s)). Since

$$\dot{m} = \rho \cdot F = \rho \cdot u \cdot A \quad (5)$$

where  $A$  (m<sup>2</sup>) is the cross section of the tube,  $Re$  can be rewritten for a circular tube as

$$Re_{av} = \frac{4 \cdot \dot{m}}{\mu_{av} \cdot \pi \cdot d_{tub}} \quad (6)$$

Since the viscosity changes with pressure along a tube, a length-averaged Reynolds number and viscosity are introduced. An example of the calculation of  $Re$ , based on a velocity or mass flow rate, is given in the Supplementary Information.

The Reynolds number for a column packed with particles,  $Re_p$ , using the introduced mass flow rate above, can be defined as [8]

$$Re_p = \frac{d_p \cdot \dot{m}}{\mu_{av} \cdot A_k \cdot \epsilon_0} \quad (7)$$

where  $d_p$ ,  $A_k$  and  $\epsilon_0$  are the particle diameter, the column cross section and the external porosity. Experimental observations of solute band broadening relative to column retention have indicated

that the transition from laminar to turbulent flow occurs as  $Re_p$  increases beyond a value greater than 1 and that virtually all of the flow paths within a column become turbulent as  $Re_p$  exceeds a value of 10. [8,9] For a 4.6 mm column packed with 5  $\mu\text{m}$  particles, a  $Re_p$  is found to be equal to 0.69 (taking an external porosity of 0.4, viscosity of 0.07 cP, density of 800 kg/m<sup>3</sup> and a flow rate of 5 ml/min). Showing that no turbulent flow conditions in the column itself can be expected.

The calculation of the Darcy friction factor,  $f_D$ , is also further complicated when transition toward turbulent flow conditions occurs. Implicit as well as explicit formulas exist in these scenarios, where the friction factor is correlated to the roughness,  $\epsilon$ , of the pipe and the Reynolds number. One of the most used and universal equations ones is the so-called Colebrook–White equation, which is an implicit, semi-empirical relationship derived from experimental data on commercial rough and smooth pipes [10–12]

$$\frac{1}{\sqrt{f_D}} = -2 \cdot \log_{10} \left( \frac{\epsilon}{3.7 \cdot D} + \frac{2.51}{Re \sqrt{f_D}} \right) \quad (8)$$

The validity of this correlation was reported in the range of Reynolds numbers between 4000 and 10<sup>8</sup> and  $\epsilon/D$  between 0 and 0.05 [13]. The Colebrook–White equation requires an iterative solution procedure because the friction factor appears on both sides [14]. Explicit versions of this equation which provide a good approximation are the Haaland and Swamee–Jain equations, developed for circular pipes (i.e.  $D = d_{tub}$ ) [16,17]

$$\frac{1}{\sqrt{f_D}} = -1.8 \cdot \log_{10} \left( \left( \frac{\epsilon}{3.7 \cdot d_{tub}} \right)^{1.11} + \frac{6.9}{Re} \right) \quad (9)$$

$$f_D = 0.25 \cdot \left( \log_{10} \left( \frac{\epsilon}{3.7 \cdot d_{tub}} + \frac{5.74}{Re^{0.9}} \right) \right)^{-2} \quad (10)$$

The Haaland equation (Eq. (9)) yields values with an error below 1.5% versus the Colebrook–White equation and the Swamee–Jain (Eq. (10)) below 2% [15,13].

## 2. Experimental

### 2.1. Column, tubing and chemicals

Methanol (LC–MS grade) was purchased from Biosolve (Valkenswaard, Netherlands), CO<sub>2</sub> was purchased from Air Liquide (Paris, France). Stainless-steel (120  $\mu\text{m}$ ) and PEEK tubing (65, 100 and 127  $\mu\text{m}$ ) purchased from Achrom (Machelen, Belgium) and Viper-tubings (fused-silica, 75  $\mu\text{m}$ ) from ThermoScientific (Rucorn, Great Britain) were used. Additionally, 75  $\mu\text{m}$  stainless-steel tubing and a Zorbax 4.6 mm  $\times$  150 mm column with 5  $\mu\text{m}$  bare silica particles were purchased from Agilent Technologies (Diegem, Belgium).

### 2.2. Instrumentation and conditions

Mass flows were measured using a mini CORI-FLOW mass flow meter purchased from Bronkhorst (Olen, Belgium). The SFC-system used in the study was an Agilent Aurora SFC system with a thermostatted column compartment, autosampler with a 1.2  $\mu\text{L}$  injection loop (used in full loop mode) and a DAD-detector with a 1.7  $\mu\text{L}$  flow cell. The system was operated with chemstation. For the measurements of the pressure drop across tubing or column, two additional pressure sensors were used. For all the experiments the back pressure regulator was set at 150 bar and the oven temperature at 30 °C for all the pressure drop measurements and 40 °C for the selectivity study.

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