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Short communication

Observation of enhanced heat dissipation in columns packed with superficially porous particles

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ABSTRACT

At high flow rates and pressures, columns packed with sub-2 μm particles suffer from efficiency losses due to frictional heating. The thermal environment of the column (insulated or isothermal) can decrease or magnify these losses. While a number of studies have been conducted demonstrating the improved performance (partially due to the benefits of enhanced thermal conductivity) of columns packed with superficially porous particles, none have made a comparison between sub-2 μm fully and superficially porous particles in an isothermal environment where radial thermal gradients are maximized and thermal broadening is amplified. Here we show that when such columns are characterized in a recirculating water jacket (providing an isothermal environment), efficiency loss and changes in retention and mobile phase temperature are reduced for sub-2 μm superficially porous particles compared to sub-2 μm fully porous particles.

1. Introduction

The problems associated with viscous heating at high flow rates in HPLC have been well known for decades [1–3]. Heat is generated in a column because of the friction of liquid flowing through a bed of packed particles [4,5]. This leads to the formation of axial temperature gradients along the length of the column (the temperature is warmer at the outlet than the inlet) as well as radial temperature gradients (the fluid at the center of the column cross section is warmer than the fluid at the walls). The rate of heat generation, or power, is equal to the product of the flow rate (F) and pressure drop (ΔP) [6]:

$$\text{Power} = F\Delta P \quad (1)$$

In HPLC, column flow rates near the optimal mobile phase velocity are usually in the range of 1–2 mL/min (in a 4.6 mm diameter column) using 3–5 μm particles. To avoid excessive heating, the pressure limit for nearly all HPLC instruments was set at 400 bar [7]. When this pressure limit was first exceeded ten-fold in UHPLC, frictional heating generated by flowing mobile phase through a bed of sub-2 μm particles was avoided by using capillary columns [6,7]. The lower flow rates (100–300 nL/min) only generated power in the mW range (as opposed to the Watts that would be generated in a 4.6 mm diameter column) and the larger surface area-to-volume ratio allowed for better heat dissipation. When UHPLC was initially commercialized as UPLC by Waters Corporation, a compromise between these two ranges was made where column diameter was decreased by half (giving optimal mobile phase velocities for sub-2 μm particles at flow rates in the 0.2–1 mL/min) and the pressure limit was more than doubled over HPLC (up to 1000 bar) [8]. At lower flow rates and pressures in this range viscous heating is negligible but becomes problematic as the pressure limit is approached at higher flow rates. The rapid adoption of these columns in the separations community has led to a renewed interest in understanding how this heating impacts chromatographic efficiency [9–12].

An important step forward in LC stationary phase technology came in 2006 with the wide release of columns packed with superficially porous particles (SPPs) [13]. Multiple studies have compared sub-2 μm fully porous particles (FPPs) and SPPs and concluded that broadening due to thermal effects is lower in columns packed with SPPs [14–16]. A chromatographic bed packed with SPPs is calculated to have a thermal conductivity over twice that of a bed packed with FPPs when acetonitrile is used as the mobile phase [14,15]. This increase is attributed to the solid silica core found in the SPPs which increases the volume fraction of the silica (the thermal conductivity of silica is 1.4 W/m/K while that of acetonitrile is 0.2 W/m/K) [15]. In addition to the particle structure, the thermal environment of the column can impact the broadening due to frictional heating. In an insulated column oven (which can replicate a quasi-adiabatic system) thermally induced efficiency losses

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are reduced [17] while thermally induced broadening increases in isothermal environments (such as columns maintained in a re-circulating water bath [9,17,18] or a forced-air convection oven [10]). To our knowledge, no studies have been reported in the literature comparing the effects of thermal conductivity differences between FPPs and SPPs in an isothermal system when the radial thermal gradient is most detrimental to column performance. To that end, this communication details such a comparison (where the radial thermal gradient was purposely maximized by using a re-circulating water bath). The results presented here are the first direct and unambiguous experimental demonstration of the significantly superior thermal conductivity of superficially porous particles over totally porous particles.

2. Materials and methods

2.1. Temperature control and measurement

To create an isothermal environment for the column, a water flow jacket consisting of a 3/4″ diameter (5/8″ inner diameter) glass tube with two tube connectors constructed by the UNC Glass Shop (replicating a design described in [9]). Approximately 2–3 L/min recirculating water flow was supplied to the jacket by a M60A submersible aquarium pump (Beckett, Norfolk, VA) placed in a large insulated beverage cooler filled with water that was temperature controlled to 300 K using a Fluval M-100 submersible glass aquarium heater (Hagen, Mansfield, MA).

Column mobile phase temperature measurements were made at the outlet using a Type-T (Copper-Constantan) HYP-0 mini-hypodermic (0.008″ diameter) thermocouple probe (Omega Engineering, Stamford, CT) inserted into a 1.5 cm segment of 0.015″ inner diameter PEEK tubing (Idex Health and Science, Oak Harbor, WA) based on a previously reported method [21]. The thermocouple probe was positioned into the tubing segment so that the end was adjacent to the outlet frit. Thermocouple data was acquired using a OM-EL-USB-TC USB Thermocouple Data Logger with Easy-Log USB software (Omega Engineering, Stamford, CT). For each new flow rate, the temperature was measured following an equilibration period (a stable temperature was reached following each change in flow rate) and then compared to the power generated as calculated by using the pressure displayed by the instrument software and Eq. (1). The temperature for columns packed with both particle types was measured (relative to the eluent temperature measured at a flow rate of 10 μL/min where frictional heating would be negligible) with the column in still air while resting in the column oven (which had to be open due to the positioning of the thermocouple probe) and with the column placed in the flowing water jacket. When the experimental temperature data was plotted, linear fits were applied as guides to the eye and are not an implication of a strictly linear relationship between temperature and power.

2.2. Chromatographic columns and instrumentation

2.1 × 150 mm stainless steel columns (with identical column bodies and endfittings) containing sub-2 μm particles were prepared by Waters Corporation (Milford, MA). 150 mm length columns were used to ensure the bed length was greater than the thermal entrance length [11,17] and that thermal gradients were fully developed at all flow rates used. The FPPs were Waters 1.8 μm HSS T3 and the SPPs were 1.6 μm Waters prototype material similar to the commercially available CORTECS columns. A Waters Acquity UPLC system (Milford, MA) was used for all experiments. The instrument is equipped with a Binary Solvent Manager that can generate pressures up to 15,000 psi and flow rates up to 2.0 mL/min.

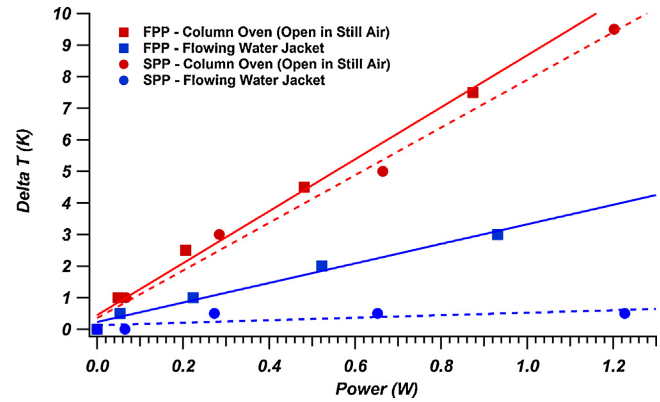

Fig. 1. Temperature change values (measured using a hypodermic thermocouple probe at the column outlet) compared to generated power (calculated by Eq. (1)) for 2.1 × 150 mm FPP and SPP columns set in the open instrument column oven and inside the isothermal environment of a recirculating water jacket. Linear fits to the experimental data (solid lines for FPPs and dotted lines for SPPs) are included solely as a guide to the eye.

The Acquity Sample Manager includes a six-port injection valve (these experiments utilize the partial loop with needle overfill injection mode for 1 μL injections) and an insulated column oven (set at 303 K). Optima LC-MS grade acetonitrile (Fisher Scientific, Fair Lawn, NJ) was used as a mobile phase. Acetonitrile was selected as the mobile phase to ensure low viscosity in order to reach higher flow rates at the instrument pressure limit, thus maximizing the thermal load. The analyte used for efficiency measurements was hexadecanophenone (TCI America, Portland, OR) with thiourea (Sigma Chemical Company, St. Louis, MO) serving as a dead time marker. Flow rates ranged from 50 to 900 μL/min. Between each change in flow rate, the column was equilibrated for at least 10 min to ensure stable temperatures (and reduce effects due to the column's thermal history). A Waters PDA Detector was used for analyte detection (chromatograms were collected at 254 nm). The data acquisition rate was set from 10 to 80 Hz to ensure at least 40 points were collected per peak in all experiments. Plate counts were measured using an iterative statistical moments method to determine the hexadecanophenone peak's second central moment (variance) [19]. Reduced plate heights were then calculated using the particle diameters listed above while reduced velocities were calculated with the observed column dead time and diffusion coefficients from the Wilke–Chang equation [20]. Peak variance was corrected for extra-column broadening effects by subtracting the system variance measured when the column was replaced with a zero-dead volume fitting from Valco (Houston, TX).

3. Results and discussion

3.1. Differences in temperature effects between columns

To track how viscous heating affected the temperature profile of the different particle types, a method from a previous study [21] using a hypodermic thermocouple probe for outlet mobile phase temperature measurements was utilized. In Fig. 1, the FPP and SPP columns have similar temperature vs. power plots (power calculated by Eq. (1)) in still air because of the near-adiabatic conditions and the dominant effects of the stainless steel column body and end fittings (that are identical in both columns) which can affect thermal gradients [21]. However, when the water jacket is used to increase heat removal from the column, differences between the particle types are revealed. While the FPP column has a temperature increase of 3 K at 0.9 W of generated power, the SPP column only shows an increase of 0.5 K up to 1.2 W. This means that the heat