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Measurement of the axial and radial temperature profiles of a chromatographic column
Influence of thermal insulation on column efficiency

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Abstract

The temperatures of the metal wall along a chromatographic column (longitudinal temperature gradients) and of the liquid phase across the outlet section of the column (radial temperature gradients) were measured at different flow rates with the same chromatographic column (250 mm ×4.6 mm). The column was packed with 5 μm C_{18}-bonded silica particles. The measurements were carried out with surface and immersion thermocouples (all junction Type T, ±0.1 K) that measure the local temperature. The column was either left in a still-air bath (ambient temperature, $T_{\text{ext}} = 295$–296 K) or insulated in a packing foam to avoid air convection around its surface. The temperature profiles were measured at several values of the inlet pressure ($\simeq$ 100, 200, 300 and 350 bar) and with two mobile phases, pure methanol and a 2.5:97.5 (v/v, %) methanol:water solution. The experimental results show that the longitudinal temperature gradients never exceeded 8 K for a pressure drop of 350 bars. In the presence of the insulating foam, the longitudinal temperature gradients become quasi-linear and the column temperature increases by +1 and +3 K with a water-rich (heat conductivity $\simeq$ 0.6 W/m/K) and pure methanol (heat conductivity $\simeq$ 0.2 W/m/K), respectively. The radial temperature gradients are maximum with methanol (+1.5 K at 290 bar inlet pressure) and minimum with water (+0.8 K at 290 bar), as predicted by the solution of the heat transfer balance in a chromatographic column. The profile remains parabolic all along the column. Combining the results of these measurements (determination of the boundary conditions on the wall, at column inlet and at column outlet) with calculations using a realistic model of heat dispersion in a porous medium, the temperature inside the column could be assessed for any radial and axial position.

Keywords: Chromatographic column; Temperature profiles; Longitudinal and radial temperature gradients; Mobile phase heat conductivity; C_{18}-bonded silica; Mobile phase; Methanol; Water

1. Introduction

Since the inception of HPLC, chromatographic columns have been packed with smaller and smaller particles, leading to dramatic reductions in analysis times. After a period in the 1980s and 1990s, when most analytical columns were packed with 4 or 5 μm silica particles, the race toward the use of smaller particles has started again. Packing shorter columns with finer particles (now $d_p < 2$ μm) allows a further important decrease of analysis times, the reason for these shorter analysis times being that the optimum mobile phase velocity increases with decreasing particle diameter [1]. As a matter of fact, the optimum reduced velocity and the minimum column HETP are such that $\nu_{\text{opt}} \propto d_p^{-1}$ and $H_{\min} \propto d_p$. Unfortunately, high flow rates require the use of ultra-high column inlet pressure (> 1 kbar) [2,3] because the column permeability, k_0, decreases as the square of the particle diameter ($k_0 \propto d_p^2$). Thus, the race toward using smaller particles can be pursued only as long as: (1) the instrument contributions to band broadening are drastically controlled and (2) pumps delivering mobile phases at very high pressures are available. Conventional equipment cannot operate at inlet pressures exceeding 400 bar. To withstand higher pressures, specially designed and built pumps, valves and connecting tubes are needed. Packing shorter columns with smaller diameter particles alleviates the problem to some extent. Much faster analyses are possible but at the cost of a reduced efficiency.

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While classical columns are packed with 4–5 μm particles and have lengths ranging between 15 and 30 cm, modern columns are packed with 1.5 μm particles and have lengths of 3 cm. The former provide 15–30,000 plates; the latter barely 10,000 but the analyses are about 30 times faster.

To achieve both fast and highly efficient separations, it becomes necessary to operate columns at pressures in the range of 1–2 kbar. Then, however, the compression of the mobile phase stores in the liquid an important amount of energy. This energy is released in the column during the decompression of the mobile phase. It is degraded into heat by the viscous friction. The amount of energy stored increases with increasing pressure. Its release generates a power that increases with decreasing column length and particle size, and with increasing inlet pressure and flow rates (all parameters that are closely related). The release of this energy increases the local temperature and causes a temperature gradient along the chromatographic column and, unless the column is well insulated thermally, a temperature gradient across the column, due to heat exchanges with the outside atmosphere. Both gradients may affect drastically the column HETP and limit the efficiency of chromatographic columns [4,5]. Theoretical calculations of temperature profiles were made in the 1980s [6,7]. They predict the intensities of both longitudinal and radial temperature gradients. The consequences of these gradients are that the adsorption properties of the packing material are uniform neither along the column nor over its cross-section. So, the values measured for the retention factors and for all the thermodynamic functions related to them are average and may be most difficult to account for since their temperature dependence is exponential, not linear.

More specifically, the viscosity of the mobile phase changes across the column section, solvents being less viscuous in the central zone, where they are warmer, than in the region near the wall, where they are colder. The mobile phase being isobaric over the column cross-section under steady state, the local mobile phase velocity will be higher in the column center than close to its wall. So, sample bands propagate faster in the central region of the column than in the region close to its wall. This causes a severe loss of efficiency as any radial heterogeneity [4–10]. The radial temperature heterogeneity causes also the components that are in the center of the column to be less strongly adsorbed, hence less retained, and to move faster not only because the mobile phase moves faster but mostly for this reason [5]. Finally, when applying a concentration gradient (such as a solvent gradient), one might expect to observe also a gradient of concentration along the column radius, not simply along the column length since the solvent moves more slowly along the column wall. This effect adds up to the different consequences of the friction heat generation.

In spite of considerable theoretical efforts, the practical consequences of the temperature heterogeneity of chromatographic columns on their HETPs and their velocity dependencies have not yet been clarified. In the 1970–1980s, Lin and Horváth [6], Poppe and Kraak [7] and Halasz et al. [9] proposed models for the viscous dissipation of energy in packed beds, studied the influence of the thermal conditions on the efficiency of HPLC columns, and demonstrated the effect. Recent experimental results have confirmed it [8]. However, further theoretical and experimental studies need to be done because the available models do not take properly into account the simultaneous effects of the longitudinal and the radial temperature gradients. No general HETP equation can predict accurately HETP data curves under non-isothermal steady-state conditions. Friction effects occuring in the chromatographic column ends up to be a serious limitation to the increase of the speed and efficiency of HPLC separations.

In this work, we aimed at measuring the temperature profiles of fluids percolating through a given chromatographic column under various sets of steady-state conditions (constant pressure drop or constant temperature gradients). The temperatures were measured along the external surface of the column wall. The radial temperatures were measured immediately downstream the frit placed at the column outlet. A complete temperature map inside the chromatographic column will be derived from a dynamic model of heat dispersion in a chromatographic column [6], when the temperature of the column wall is not uniform.

2. Theory

2.1. Propagation of heat in a chromatographic bed without temperature wall control

Without loss of generality, the heat balance equation is written in the assumption of cylindrical symmetry for heat dispersion through the chromatographic column and for heat exchanges across the wall. Accordingly, the temperature profile $T = T(r, z)$ of the column is a function of the radial coordinate r and the column length z. Let consider a volume element of column between the longitudinal coordinates z and $z + \mathrm{d}z$ and between the radial coordinates r and $r + \mathrm{d}r$ (Fig. 1). In this treatment, we assume, as a first approximation, that the mobile phase is not compressible, which is a reasonable first approximation for

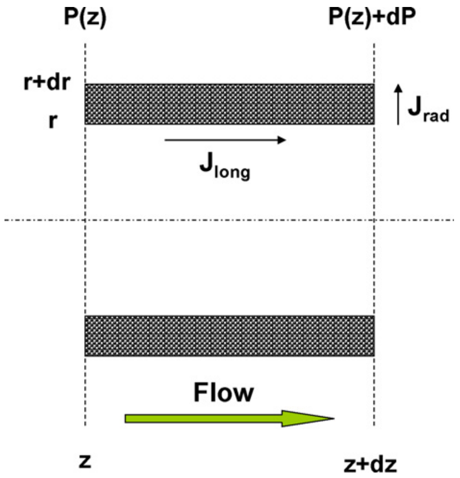

Fig. 1. Longitudinal section of the column between the axial positions z and $z + \mathrm{d}z$. The symmetry of the heat dispersion problem imposes the elementary volume of the column included between the radial coordinates r and $r + \mathrm{d}r$. Three distinct heat fluxes must be considered into the heat balance equation: one radial (diffusion J_{rad}), one longitudinal (diffusion J_{long}) and one by convection in the direction of the flow.