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Quasi-adiabatic vacuum-based column housing for very high-pressure liquid chromatography

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ABSTRACT

A prototype vacuum-based (10^{-6} Torr) column housing was built to thermally isolate the chromatographic column from the external air environment. The heat transfer mechanism is solely controlled by surface radiation, which was minimized by wrapping the column with low-emissivity aluminum tape. The adiabaticity of the column housing was quantitatively assessed from the measurement of the operational pressure and fluid temperature at the outlet of a 2.1 mm × 100 mm column (sub-2 μm particles). The pressure drop along the column was raised up to 1 kbar. The enthalpy balance of the eluent (water, acetonitrile, and one water/acetonitrile mixture, 70/30, v/v) showed that less than 1% of the viscous heat generated by friction of the fluid against the packed bed was lost to the external air environment. Such a vacuum-based column oven minimizes the amplitude of the radial temperature gradients across the column diameter and maximizes its resolving power.

1. Introduction

Very high-pressure liquid chromatography (vHPLC) significantly improved the resolution power of traditional LC (column back pressure <400 bar) in the mid-2000s. High-strength sub-2 μm fully porous particles were successfully prepared and high-pressure pumps enabled analysts to apply flow rates of a few mL/min at pressures around 1 kbar [1–4]. 5 cm long narrow-bore columns packed with sub-2 μm may generate the same plate number as that of 15 cm long column packed with 5 μm particles. The main advantage of vHPLC over classical LC is the noticeable reduction of the analysis time by one to two orders of magnitude.

vHPLC may have two downsides if precautions are not properly taken by the analyst. First, the amount of bandspreading taking place in the vHPLC system should be minimized in order to maximize the resolution level of short, narrow-bore columns packed with fine particles [5–11]. The volumes of the injection device, connecting tubes, detection cell, and of the column frits have to be reduced without sacrificing sensitivity and analysis speed. Additionally, the connections between these parts have to be handled carefully. Second, the amount of viscous heat generated by the friction of the eluent flowing through the packed bed can be substantial with 2.1 or 3.0 mm i.d. column run at maximum allowable velocities [12–19]. Under steady state temperature regime, this heat generates radial temperature gradients that may cause serious losses of column efficiency [18,20–24]. The analyst should take all the necessary precautions that will eventually minimize heat losses through the column wall. Solutions may consist of wrapping the column with some isolating foam [19,25,26], housing the column in a tube heater matching the expected axial temperature profile [27], or in minimizing the persistence length of radial temperature gradients expected along the column by applying intermediate eluent cooling [28]. However, all these practical answers to the problem of vHPLC band broadening due to viscous heating only partially eliminate heat fluxes controlled by natural convection, conduction, or radiation.

Using 3 kbar liquid pumps together with 2.1 mm i.d. columns packed with 1 μm particles would generate even more viscous heat and cause significant losses in column efficiency. In regards to 2.1 mm i.d. columns packed with 1.7 μm particles currently run at 1 kbar, the heat power would be multiplied by about a factor 5. In order to maintain the robustness of the retention times (controlled by the amplitude of the axial temperature gradient) and the resolution power (controlled by the amplitude of the radial temperature gradient) of this next generation of vHPLC columns, a strict control of the thermal environment surrounding the chromatographic column would become necessary. In a recent report [29], it was shown that most of the heat power lost at the column wall could be eliminated by applying a high vacuum ($<10^{-5}$ Torr) around the whole column. The relative increases of the

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efficiency of 2.1 mm × 100 mm columns packed with 1.8 μm particles were measured at 30% (0.6 mL/min, 10 500 psi pressure drop, acetonitrile/water eluent mixture, 50/50, v/v) and 45% (0.7 mL/min, 11 000 psi pressure drop, acetonitrile/water eluent mixture, 70/30, v/v). It was demonstrated that the reduction of the amplitude of the radial temperature gradients using quasi-adiabatic ovens improves the uniformity of the flow anastomosis across the column diameter.

In this work, we investigate the adiabaticity level of a prototype high-vacuum column housing. At such a low pressure around 10^{-5} Torr, natural convection is fully eliminated because air molecules obey a molecular flow regime [29]. Additionally, the thermal conductivity of air is reduced by nearly three orders of magnitude making air conduction virtually negligible. Therefore, the heat transfer between the chromatographic column and the external environment is essentially controlled by electromagnetic radiation. To minimize thermal radiation, the column may be wrapped with some low-emissivity aluminum tape. The adiabaticity of the high-vacuum column housing is directly measured for three different eluents (100% water, acetonitrile/water mixture, and 100% acetonitrile) based on the change of the temperature and enthalpy of the fluid percolating through the porous column. The experimental effects of the nature of the eluent and of the column back pressure on the adiabaticity level of the high-vacuum column housing is reported, discussed, and compared to those of classical still-air column oven.

2. Theory

2.1. Basic thermodynamic relationships

In this work, we will focus on the state function enthalpy, H, of a fluid percolating under steady state regime through a vHPLC column. H is conserved when the fluid decompression is performed adiabatically [30]. For a closed system (no chemical energy is added to the system, $dN = 0$), the two natural variables of H are the extensive state function entropy, S, and the intensive variable pressure, P. The differential of H with respect to entropy and pressure changes is written [30]:

$$dH = TdS + VdP \tag{1}$$

where T denote the intensive variable temperature.

Since the fluid entropy cannot be measured directly, the thermal coefficients h_T and h_P are introduced in order to express the enthalpy differential as a function of the temperature and pressure changes (dT and dP), which are both easily accessible experimentally. Accordingly, by definition

$$dH = h_T dT + h_P dP \tag{2}$$

The thermal coefficients h_T and h_P need to be determined from the first law of thermodynamics and from the mathematical properties of total differential functions (or state functions). The entropy is a state function, so, its differential can be written:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{3}$$

$$= \frac{dQ}{T} \quad \text{(definition of reversible transformation)} \tag{4}$$

$$= \frac{C_p}{T} dT + \frac{h}{T} dP \quad \text{(definition of } dQ\text{)} \tag{5}$$

where dQ is the heat exchanged between the fluid and the external environment during a reversible transformation, C_p (>0) is the heat capacity of the fluid at constant pressure, and h (<0) is the amount of heat released by the fluid to the external environment per unit increase of pressure at constant temperature.

A relationship can be found between the thermal coefficient h and the heat capacity C_p based on the equality of the second cross partial differentials of S:

$$\frac{\partial^2 S}{\partial P \partial T} = \frac{\partial^2 S}{\partial T \partial P} \leftrightarrow \left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial h}{\partial T}\right)_P - \frac{h}{T} \tag{6}$$

From the first principle of thermodynamics,

$$dH = dU + d(PV) \quad \text{(definition of enthalpy)} \tag{7}$$

$$= dQ - PdV + PdV + VdP \quad \text{(first principle of thermodynamics)} \tag{8}$$

$$= C_p dT + (h + V)dP \quad \text{(definition of } dQ\text{)} \tag{9}$$

First, by identification of Eq. (2) with Eq. (9), the thermal coefficient h_T is equal to the heat capacity of the fluid at constant pressure. So, $h_T = C_p$. Similarly, the second thermal coefficient is $h_P = h + V$.

Secondly, the expression of the variable h is derived from the equality of the second cross partial differentials of the state function H in Eq. (9):

$$\frac{\partial^2 H}{\partial P \partial T} = \frac{\partial^2 H}{\partial T \partial P} \leftrightarrow \left(\frac{\partial C_p}{\partial P}\right)_T = \left(\frac{\partial h}{\partial T}\right)_P + \left(\frac{\partial V}{\partial T}\right)_P \tag{10}$$

Identification of Eq. (6) with Eq. (10) leads to the expression of h. Accordingly, the expression of the thermal coefficient h_p becomes:

$$h_p = h + V \tag{11}$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_P + V \tag{12}$$

$$= V(1 - \alpha T) \tag{13}$$

where α is the thermal expansion coefficient of the fluid at constant pressure defined by:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{14}$$

2.2. Steady state fluid decompression

The eluent percolating through the chromatographic column is assumed to decompress under a steady state regime. The goal is to measure the level of adiabaticity of the column oven compartment under this condition. The experimental values of the inlet and outlet eluent temperatures (T_i and $T_{o,exp}$), and those of the inlet and outlet pressures (P_i and P_o) are easily accessible with thermocouples and pressure sensors.

The adiabaticity level of a column oven may be defined as the ratio, q_T, of the observed difference between the outlet and inlet temperature of the eluent ($T_{o,exp} - T_i$) to the same expected temperature difference ($T_{o,adiabatic} - T_i$), would the column be operated under strict adiabatic conditions:

$$q_T = \frac{T_{o,\exp} - T_i}{T_{o,adiabatic} - T_i} \tag{15}$$

Accordingly, for a perfectly adiabatic oven, q_T=1. For the sake of reference, if the column is immersed in a thermal environment such as $T_{o,exp} = T_i$, then, $q_T = 0$. If the column is placed under forced convective air conditions, then, $q_T < 0.5$ [31]. If the column is placed under classical still-air conditions, then, $q_T \sim 0.7$ [18].

The adiabaticity of the column oven compartment may also be defined as the ratio, q_P, of the amount, $\dot{Q}$, of heat power released by the fluid to the external environment to the total viscous heat power, $P_f = F_v \Delta P$, irreversibly produced by the friction of the fluid layers against the packed bed [12,19]. $\dot{Q}$ can be directly measured