



# Pressure, temperature and density drops along supercritical fluid chromatography columns in different thermal environments. III. Mixtures of carbon dioxide and methanol as the mobile phase



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## ABSTRACT

The pressure, temperature and density drops along SFC columns eluted with a CO<sub>2</sub>/methanol mobile phase were measured and compared with theoretical values. For columns packed with 3- and 5- $\mu$ m particles the pressure and temperature drops were measured using a mobile phase of 95% CO<sub>2</sub> and 5% methanol at a flow rate of 5 mL/min, at temperatures from 20 to 100 °C, and outlet pressures from 80 to 300 bar. The density drop was calculated based on the temperature and pressure at the column inlet and outlet. The columns were suspended in a circulating air bath, either bare or covered with foam insulation. The experimental measurements were compared to theoretical results obtained by numerical simulation. For the convective air condition at outlet pressures above 100 bar the average difference between the experimental and calculated temperature drops and pressure drops were 0.1 °C and 0.7% for the bare 3- $\mu$ m column, respectively, and were 0.6 °C and 4.1% for the insulated column. The observed temperature drops for the insulated columns are consistent with those predicted by the Joule–Thomson coefficients for isenthalpic expansion. The dependence of the temperature and the pressure drops on the Joule–Thomson coefficient and kinematic viscosity are described for carbon dioxide mobile phases containing up to 20% methanol.

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## 1. Introduction

The retention of a solute in elution chromatography is controlled by the properties of the solute and the stationary phase, by the properties and composition of the mobile phase, by the relative amounts of the two phases, and by the temperature. In general, the primary parameters available for control by the operator are the mobile phase composition and its flow rate, and the temperature. In GC the mobile phase itself does not affect retention, and the only operator variables are the temperature and flow rate. Changes in the flow rate are accompanied by an increase in the inlet pressure in both GC and HPLC, which has no effect on the retention factor except at extremely high pressures. In SFC the retention is controlled not only by the mobile phase composition and the temperature, but also by the density of the mobile phase. The density is a property of the mobile phase that depends on its temperature

and pressure, and these parameters can be controlled directly by the operator. Among the three principle forms of chromatography, it is only in SFC that pressure has a strong effect on retention.

The importance in SFC of the mobile phase composition, its temperature, and its pressure in controlling retention has been well documented. With neat CO<sub>2</sub> mobile phase the retention generally decreases monotonically with increasing density [1–4]. Because the mobile phase density is controlled by the temperature and pressure, these two latter parameters, along with the mobile phase composition, are used as operator variables to control retention in SFC separations.

The success of a chromatographic separation depends not only on selective retention, but also on the column efficiency, which is controlled largely by the structure of the column bed and by the mass transport properties of the mobile phase. A key parameter affecting the efficiency is the velocity of the mobile phase, which depends on its mass flow rate and its density. The density varies with the temperature and pressure, and the pressure decreases along the column, resulting in a decrease in its density along the column and a corresponding increase in the volumetric flow rate and

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linear velocity. This expansion of the mobile phase can be accompanied by a decrease in its temperature, resulting in axial and radial temperature gradients [5–8]. If these temperature gradients are large enough, they can cause radial gradients of the mobile phase viscosity, hence of its velocity and significant loss of efficiency. In addition to the velocity, gradients in the solute diffusion coefficients as well as in the retention factors develop. The importance of axial and radial temperature gradients in both UHPLC and SFC have been treated in a recent review [9].

It is clear from the preceding discussion that a complete description of the retention and efficiency in packed SFC columns requires detailed information about the pressure, temperature and density variations along and across the column. Although the effect of pressure drop on density variations is well understood, the significance of temperature changes along SFC columns was not fully appreciated until recently. An early treatment of pressure, density and temperature profiles in 1987 concluded that temperature gradients were not a significant concern in SFC [8]. These results were based on numerical calculations that employed the IUPAC equation of state for carbon dioxide for columns packed with particles with diameters from 4 to 10  $\mu\text{m}$ , and with pressure drops up to 12 bar. The largest predicted temperature drop at inlet pressures below 100 bar was less than 0.2  $^{\circ}\text{C}$ . At inlet pressures of 150 bar small increases in the temperature were predicted for inlet temperatures below 50  $^{\circ}\text{C}$ . No experimental measurements were reported. More than 20 years later Poe and Schroden [7] reported much larger temperature drops for columns packed with 3-, 5-, and 10- $\mu\text{m}$  particles and operated with neat carbon dioxide. The largest temperature drop reported was 15  $^{\circ}\text{C}$  for a column packed with 3- $\mu\text{m}$  particles. Further experimental and theoretical studies have demonstrated that for essentially all operating conditions commonly used in SFC a substantial temperature drop exists, typically on the order of several degrees Celsius [10,11]. Several recent articles [5,6,12,13] have described models for SFC that take these variations into account. However, they do not present a general analysis of these variations in terms of their impact on the resulting temperature, pressure and density drops along the column. In this paper we provide a detailed examination of these phenomena that should provide useful information for the rational design of efficient SFC separations.

This paper is an extension of previous work on the pressure, temperature and density drops in SFC columns [10,11,14,15]. In two of those papers [14,15] we presented calculated results for the pressure and density drops for columns operated under isothermal conditions using  $\text{CO}_2$  with and without added methanol. These calculations showed the complex dependencies of these parameter drops on the operating temperature and pressure and offer useful information for the design and interpretation of SFC separations when conducted under conditions where the temperature drop is small and can be neglected. In other papers [10,11] we presented results for these parameter drops for columns operated with neat  $\text{CO}_2$  mobile phase, which included and compared experimental and calculated data for the temperature drops along columns operated in different thermal environments.

Most SFC separations are not done using neat  $\text{CO}_2$ , but with a solution in  $\text{CO}_2$  of a polar modifier, most commonly methanol. This modifier is added primarily to increase the solubility of the solutes in the mobile phase and to decrease the retention of polar solutes. It also increases the viscosity and modifies other properties that can affect the pressure, temperature and density drops along a column. In this part of the study, we measured these parameter drops on columns packed with 5- and 3- $\mu\text{m}$  particles using a mixture of 95%  $\text{CO}_2$  and 5% methanol (v/v) over a wide range of temperatures and pressures. We also performed numerical simulations to validate a theoretical model that can accurately describe the pressure,

temperature and density distributions along SFC columns using methanol-modified mobile phase.

## 2. Theoretical models

To model the temperature, pressure and density drop we have used the two dimensional model of heat transfer, coupled with a model of mobile phase velocity distribution – Model I described in [10]. This model describes variations in these parameters in both the axial and radial directions. To avoid very long computation time in the case of insulated column the boundary condition (6c) in [10] for  $r = R_e$  was modified, namely the layer of insulator was removed from the model and Eq. (6c) was replaced by boundary condition (6c'):

$$\lambda_w \frac{\partial T(r, z)}{\partial r} = h'_e (T_{\text{ext}} - T(r, z)); \quad \text{boundary condition} \quad (1)$$

where  $\lambda_w$  is the thermal conductivity of the column wall,  $T$  is temperature,  $T_{\text{ext}}$  is the external air temperature in the oven,  $r$  and  $z$  are the axial and radial positions, and  $R_e$  is the radial position of the external surface of the metal wall of the column. The effective heat transfer coefficient was calculated from the formula

$$h'_e = \frac{1}{d_2(1/(\beta d_3) + (\ln(d_3/d_2))/2\lambda_i)} \quad (2)$$

In this equation the  $d_2 = 2R_e$  is the internal insulator diameter,  $d_3$  is the external insulator diameter,  $\beta$  is the heat transfer coefficient from the surface of the insulator to the air outside the column and  $\lambda_i$  is the heat conductivity of the insulator.

For a stationary state of heat transfer process, the solution of the heat transfer Model I with boundary condition (6c') gives identical solution as the model in which the insulator layer is explicitly taken into account. However, the time of computation is several times shorter. The physico-chemical properties of the  $\text{CO}_2$ -methanol mobile phase were calculated using procedures implemented in the program REFPROP 9.0 of the United States National Institute of Standards and Technology (NIST) [16].

## 3. Experimental work

### 3.1. Experimental conditions and measurements

The experimental work was described in detail in an earlier paper [11]. In this section we provide a brief summary of the experimental conditions.

A Hewlett-Packard SFC model HP G1205A with the injector and detector removed from the flow path was used for this study. The pressure was measured to the nearest 0.1 bar at tees installed near the column inlet and outlet. In order to minimize the extra-column contributions to the pressure drop, all the connections were made using 0.75-mm i.d. tubing and fittings. Digital thermometers, calibrated against a NIST traceable standard device, were used to measure the temperatures of the oven and the column end fittings to within  $\pm 0.1$  K. A tempering unit, consisting of a 0.5-m length of 0.75-mm i.d. tubing sandwiched between two aluminum blocks plus an additional 1-m length of 0.75-mm i.d. tubing, was installed inside the oven to bring the temperature of the incoming mobile phase to within 0.1  $^{\circ}\text{C}$  of the oven temperature.

The pressure and temperature drops for two Interchrom 4.6-mm i.d. columns from Interchim were measured using 95%  $\text{CO}_2$ /5% methanol (v/v) at a volumetric flow rate of 5.00 mL/min. One column was 250 mm long and packed with 5- $\mu\text{m}$  porous silica particles designated as RP44-C18, the other 150 mm long and packed with 3- $\mu\text{m}$  Strategy 3 C18-3 particles. The columns were suspended in the oven of the Hewlett-Packard SFC system with the fan running, with the column either bare or covered with foam insulation

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