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## Adiabatic packed column supercritical fluid chromatography using a dual-zone still-air column heater

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### ABSTRACT

An approach to conducting SFC separations under pseudo-adiabatic condition utilizing a dual-zone column heater is described. The heater allows for efficient separations at low pressures above the critical temperature by imposing a temperature profile along the column wall that closely matches that for isenthalpic expansion of the fluid inside the column. As a result, the efficiency loss associated with the formation of radial temperature gradients in this difficult region can be largely avoided in packed analytical scale columns. For elution of n-octadecylbenzene at 60 °C with 5% methanol modifier and a flow rate of 3 mL/min, a 250 × 4.6-mm column packed with 5-micron Kinetex C18 particles began to lose efficiency (8% decrease in the number of theoretical plates) at outlet pressures below 142 bar in a traditional forced air oven. The corresponding outlet pressure for onset of excess efficiency loss was decreased to 121 bar when the column was operated in a commercial HPLC column heater, and to 104 bar in the new dual-zone heater operated in adiabatic mode, with corresponding increases in the retention factor for n-octadecylbenzene from 2.9 to 6.8 and 14, respectively. This approach allows for increased retention and efficient separations of otherwise weakly retained analytes. Applications are described for rapid SFC separation of an alkylbenzene mixture using a pressure ramp, and isobaric separation of a cannabinoid mixture.

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### 1. Introduction

The ability to use temperature and pressure to optimize a chromatographic separation is often touted as a major advantage of SFC. In principle, as long as an analyte remains soluble in the mobile phase, any temperature and pressure can be utilized for method development in SFC if phase transitions are avoided and the retention factor is reasonable [1]. Unfortunately, the full utilization of temperature and pressure as method variables has been limited due to problematic thermal effects that arise as the mobile phase decompresses along the chromatographic column. These thermal effects, which are described in greater detail in the following paragraphs, can include severe losses of efficiency due to the formation of radial temperature gradients associated with the decompression and cooling of the mobile phase. To avoid these problems, most SFC separations are done at relatively low temperatures, 20–40 °C, and at outlet pressures well above the critical pressure. In this

region the fluid is very liquid-like, and changes in temperature and pressure have little effect on the separation. As a result, method development in SFC described in most published work generally consists of selecting a satisfactory stationary phase and an organic modifier whose concentration is optimized to achieve the desired analyte retention, selectivity, and resolution, with little discussion provided on the selection of temperature and pressure. A few recent papers have addressed the latter topic in some detail [2–4]. Most recently, Muscat Galea et al. [4] used a response surface design approach to study the effect of temperature and back pressure on retention, separation and chromatographic efficiency, showing that the use of high temperatures and low back pressures can lead to maximal resolution of adjacent peaks.

While there are important advantages to using CO<sub>2</sub> as a mobile phase under subcritical temperatures and high pressures, there are limits to the speed and resolution that can be achieved under these conditions [5,6]. The most attractive region in terms of some important chromatographic parameters (viscosity, diffusion coefficients, method tunability) is in the supercritical region at elevated temperatures slightly above the critical pressure [5–7]. In this region retention and selectivity are more sensitive to changes in temperature and pressure, but this is also the region where drastic losses

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in chromatographic performance are generally observed [8–11]. If these efficiency losses could be avoided, SFC operations in this region would offer greater flexibility for method development, and would also offer the possibility for enhanced performance by taking full advantage of the lower viscosity of supercritical fluids.

Even as low-pressure conditions above the critical temperature offer the possibility for enhanced performance, exploration of this region has been complicated by issues that arise due to mobile phase compressibility. Recent improvements in SFC pumps have solved the issue of accurately pumping compressible fluids [12], but other issues related to fluid compressibility, especially the potential for excess efficiency loss, continue to present significant challenges to conducting operations in this region [5–9,13,14]. These issues were described in great detail in a series of papers published by Guiochon et al. [10,15–18]. The authors introduced the use of isopycnic (constant density) plots on the P-T plane to help direct method development and explain chromatographic performance for neat CO<sub>2</sub> and mixed mobile phases in SFC. They observed that performance deteriorates in the P-T region where the isopycnic lines are closely spaced. In this region, small changes in temperature and pressure result in large changes in fluid density. This is accompanied by poor heat transport and an overall lack of thermal equilibrium inside of the column [5,7,15,19]. Based on documented evidence and general arguments related to the compressibility and heat transport properties, they identified the P-T region with mobile phase densities lower than about 0.7 g/cm<sup>3</sup> as a danger zone where efficiency loss is likely to occur. More recently the Joule-Thomson coefficient of the mobile phase was shown to be a more precise guide to efficient operations in SFC [20], and is utilized in Section 3.3 of this paper.

Efficiency loss near the critical point is due primarily to the formation of radial temperature gradients inside of the column [19,21–23]. Significant cooling can occur in SFC columns packed with small particles due to expansion of the mobile phase [24–30]. This natural mobile phase cooling combined with thermostating the exterior wall of the column induces a radial temperature gradient across the column and radial distributions in important parameters such as mobile phase density and velocity, solute velocity and retention factors. The non-uniform radial distributions in these parameters cause excessive band broadening and loss of efficiency. This excess efficiency loss also occurs in HPLC due to viscous heating. Improvements in efficiency for both HPLC [31,32] and SFC [19,21–23] have been reported by using still air column heaters or thermal insulation. In addition, suspending the column in an evacuated chamber has been used to provide improved thermal isolation [33,34]. These approaches cause the column to operate in a pseudo-adiabatic environment, allowing the column wall to adopt an axial temperature profile that is similar to that of the decompressing fluid inside the column, thus minimizing the formation of radial temperature gradients.

The approaches described in the preceding paragraph have shown significant improvements for efficient SFC operations in the danger zone. However, they all rely on thermally isolating the column from its surroundings, which poses a fundamental limitation on their ability to totally eliminate the formation of radial temperature gradients under these challenging conditions. Due to the mismatch between the thermal conductivity of the packed bed and the surrounding stainless steel wall, it would be impossible to obtain an exact match in the axial temperature profiles of these two physical components of the system. In this report we describe an alternative approach for expanding the safe zones of operation in SFC to the low pressure region above the critical temperature. A dual-zone column heater is described that uses a soft heating technique to impose an axial temperature profile along the wall of the column that closely matches the profile of the mobile phase undergoing isenthalpic expansion. If the temperature

profile that is imposed on the column wall matches exactly the natural temperature profile of mobile phase undergoing isenthalpic expansion, there is no net heat exchange between the column and the external environment. This pseudo-adiabatic environment effectively prevents the formation of radial temperature gradients to improve efficiency at low outlet pressures, where the mobile phase properties and solute retention are tunable with temperature and pressure. While not strictly adiabatic, because heat can be freely exchanged between the column and the heater, we refer to this method of temperature control as “adiabatic mode” in accordance with common usage for modern chromatographic operation modes.

## 2. Experimental work

### 2.1. Equipment

#### 2.1.1. Chromatography equipment

All chromatograms were collected using a Hewlett-Packard Supercritical Fluid Chromatograph Model G1205A and a series 1050 HP diode array detector. The detector and reference wavelengths were set to 208 nm and 450 nm respectively, each with a bandwidth of 4 nm. Full loop injections were made using a Rheodyne 5092 injector with a 5- $\mu$ L injection loop. The operating system was HP-SFC Chemstation Revision A.02.02 running under Microsoft Windows 3.1.

All connections from the injector to the column and from the column to the detector flow cell were made using 0.18-mm I.D.  $\times$  1.6-mm O.D. stainless steel tubing and Valco zero-dead-volume fittings. The length of tubing from the column outlet to the detector was approximately 45 cm, and from the injector to the column inlet was approximately 70 cm.

#### 2.1.2. Temperature and pressure measurements

The pressure and temperature at various points in the system were monitored to the nearest 0.1 bar and 0.1 K respectively. The pressure transducers were Sensotec<sup>®</sup> Model TJE and had a pressure range up to 600 bar. The TJE units were calibrated against a Super TJE unit to the nearest 0.1 bar over the pressure region of interest. The inlet pressure was monitored at a tee upstream from the injector, and the outlet pressure was monitored at a tee downstream from the column outlet. The extra-column pressure drop was measured by replacing the column with 20 cm of 0.76-mm I.D.  $\times$  1.6-mm O.D. SS tubing and inserting a third pressure transducer, Sensotec Model Super TJE, into the system at this point, providing corrections for both the inlet and outlet pressure.

Small adhesive RTD probes (Omega Engineering<sup>®</sup> Model SA1) were used to monitor the temperature of the outer surface of the column. The temperature of the mobile phase was monitored by placing an adhesive RTD probe on a union approximately 5 cm upstream from the column inlet. Four RTD probes were placed on the surface of the packed section of the column at positions  $x/L = 0.20, 0.40, 0.60, 0.80$ , where  $x$  is the distance from the column inlet (where the packed section begins) and  $L$  is the column length (250 mm), and on the column end fittings to monitor the temperature profile along the column. The RTD probes were connected to an Omega OM-CP-OCTRTD data logger and were calibrated to the nearest 0.1 K against a NIST-traceable digital thermometer (Fisher Scientific) accurate to  $\pm 0.05$  K.

#### 2.1.3. Column

The column used for all experiments was purchased from Phenomenex. The column was 250 mm  $\times$  4.6 mm I.D. and was packed with superficially porous Kinetex XB-C18 particles,  $d_p = 4.60$   $\mu$ m, where  $d_p$  is the average particle size provided by the manufacturer.

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