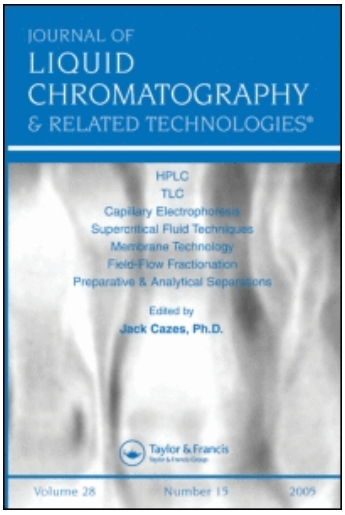

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Temperature Controlled Restrictor for Packed Capillary Column Supercritical Fluid Chromatography

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Abstract: Fatty acid methyl esters were separated by a packed capillary supercritical fluid chromatographic (SFC) column and detected by a UV detector at the wavelength of 206 nm. The temperature controlled restrictor was designed for UV detection. The temperature controlled restrictor is a 20 cm length of deactivated fused silica of 7 μm i.d., which is held right after UV detector of the packed capillary SFC. The temperature of the restrictor will control the flow rate of the supercritical carbon dioxide mobile phase through the packed capillary column in SFC. Thus, as the pressure in the column is increased during a pressure program, the temperature of 7 μm fused silica tube can be varied to maintain a constant flow rate.

Keywords: Supercritical fluid chromatography, Fatty acid methyl esters, Temperature-controlled restrictor, Packed capillary column

INTRODUCTION

The applicability of supercritical fluid is still expanding in the fields of not only chromatography but also extraction,[1] chemical reaction,[2] and environment.[3] The advantages of supercritical fluid chromatography (SFC) have recently been recognized,[4] especially capillary column supercritical fluid chromatography, although the chromatography with a supercritical fluid as mobile phase was suggested more than 40 years ago.[5]

In SFC, various types of detectors including the UV absorption detector, flame ionization detector (FID), fluorescence, refractive index, mass

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spectrometer, etc., have been used. With supercritical CO_2 and several other SFC mobile phases, it is possible to use a UV detector. In many cases, a non-destructive type detector is favourable because it is not necessary to split and waste the effluent containing sample solutes. For this reason, a UV detector is the most feasible among the detectors, which are compatible with supercritical fluids. The UV detector generally offers a stable baseline, high sensitivity, and wide linear dynamic range even with supercritical fluids. In addition, supercritical carbon dioxide is transparent even at 190 nm, which is the short wavelength limit of most of the commercial variable wavelength UV detectors.

The use of a supercritical fluid as a mobile phase requires that a flow restrictor be provided at the outlet of the column, in order to maintain the mobile phase above the critical pressures throughout the column. In the coupling of 200 μm i.d. packed capillary SFC columns with liquid chromatography (LC)-type detectors, such as the UV detector, the role of the flow restrictors is to maintain the pressure and flow rate of the mobile phase throughout the column. Three types of flow restrictors are frequently used in capillary SFC: linear restrictors,[6] tapered restrictors,[7] and integral restrictors.[8]

For most chromatographic experiments, it is very important to find the optimum variables, e.g., flow rate, temperature, and pressure, to maximize the column efficiency. SFC is no exception. The minimum height equivalent to a theoretical plate (HETP) for separations performed with open tubular capillary columns is approximately 0.7 times the column diameter. Novotny et al.[9] have shown that optimum performance in capillary SFC is achieved through the use of tubes with i.d. 50–100 μm.

For open tubular columns, the plate height (H) as a function of linear velocity (u) is expressed by the Golay equation:[10]

$$H = B/u + C_s + C_m u \tag{1}$$

In Eq. (1), C_s is the coefficient of mass transfer in the stationary phase and C_m is the coefficient of mass transfer in the mobile phase. Three contributions to band broadening, axial diffusion, resistance to mass transfer in the stationary phase, and resistance to mass transfer in the mobile phase, are all represented in Eq. (1), and can be expected to be present in SFC. In packed capillary columns, Eq. (2) is considered to be the most appropriate to describe the relationship between H and u.[11]

$$H = \frac{B'}{u} + C's\frac{k}{(1+k)^2}u + C'm\frac{1+6k+11k^2}{(1+k)^2}u \tag{2}$$

The most widely used gradient technique for SFC is pressure gradients, where the mobile phase density is altered to increase the resolution and shorten the analysis time. By steadily increasing the average pressure in the column, relatively large molecules experience an increase in solubility. This

is generally expressed as a decrease in capacity factor. This effect can be used to greatly enhance the relative molecular mass range that can be covered in a single run. As the pressure programme advances, the mobile phase flow velocity will increase as the pressure increases. It would be ideal if one could both maintain a sufficient pressure and a constant linear velocity of the mobile phase during a pressure programme. One of the most effective ways to do this is to control the restrictor temperature.[12] Increasing the restrictor temperature decreases the mass flow through capillary columns in a predictable way. Restrictor temperature programming, therefore, offers the potential for independent control of column efficiency while the pump pressure controls fluid density.[12] This paper demonstrates that this can be done effectively by the use of a temperature controlled restrictor connected after the UV detector (Fig. 1). The temperature controlled restrictor consists of a 20 cm length of deactivated fuse silica of 7 μm i.d. held in a temperature controlled environment. As the temperature of this tubing is varied, the viscosity of the fluid passing through it also changes, changing the pressure drop across the tube. The relative length, inside diameter, and temperature of the tube will control the pressure differential across its length. Thus, as the pressure in the column is increased during a pressure or density programme, the temperature of the 7 μm fused silica tube can be varied to maintain a constant linear velocity of the mobile phase.

EXPERIMENTAL

An HP (Hewlett Packard, Palo Alto, CA) Model 5890 gas chromatograph was reconstructed in the laboratory as a supercritical fluid chromatograph. This system was equipped with a C14 W loop injector (Valco) and a UV detector (Linear 203, Reno, NV, USA). SFC grade carbon dioxide (Scott

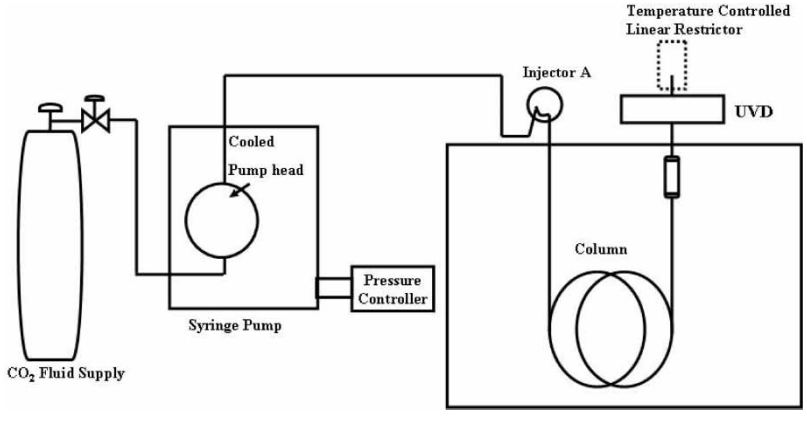

Figure 1. Schematic diagram of the packed capillary SFC/UVD system.

Specialty Gases) was used as a basic mobile phase. A 1 m × 200 μm i.d. packed capillary column was prepared with 5 μm ODS particles (Keystone Scientific, Bellefonte, PA, USA) in the laboratory. Sample volumes of 0.06 mm[3] were injected without inlet splitting with a Valco C14 W injector. The temperature controlled restrictor (20 cm × 7 μm i.d) was connected with a butt connector to the end of the UV detector.

Flow rates were measured at the end of the column using an Alltech Model 7445 flow meter. These meter monitors are the mass flow rate of the gas in the range 0–50 standard cubic centimeters per minute (SCCM). The accuracy is 2% of full scale over wide temperature and pressure ranges and the time response is 2 seconds.

RESULT AND DISCUSSION

First of all, we tried to calculate the Van Deemter curves for a packed capillary SFC system using Equation (2) introduced in an earlier session. Using the values[11] $B' = 6.15 \times 10^{-4}$, $C'_s = 0.7209$, $C'_m = 6.4 \times 10^{-3}$, and $k = 5$, the calculated Van Deemter curve is shown in Fig. 2. This Van Deemter curve can be used to predict SFC experimental conditions, e.g., with a 200 μm i.d. packed capillary column the optimum flow rate is $u = 0.06\ cm\ s^{-1}$ and the minimum plate height (HETP) is 22 μm. These curves illustrate the important point that in order to achieve the minimum HETP, the SFC experiments should be conducted with a very low linear flow velocity (about $0.06\ cm\ s^{-1}$). In reality, this is very unreasonable because the solvent peak appears about 30 min. after a sample injection

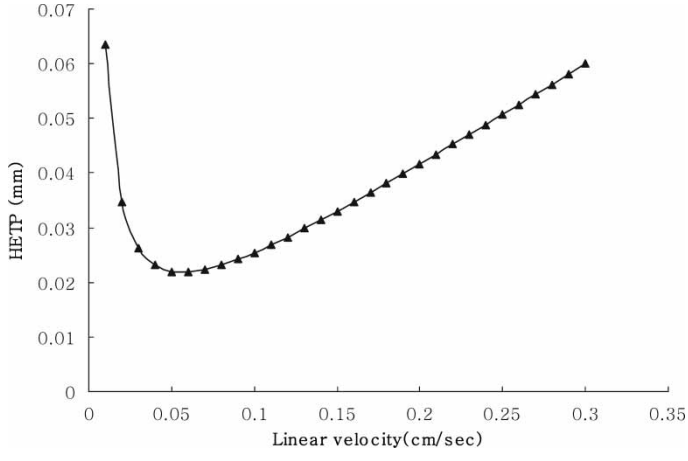

Figure 2. Van Deemter curves calculated for packed capillary SFC separations ($B' = 6.15 \times 10^{-4}$, $C'_s = 0.7209$, $C'_m = 6.4 \times 10^{-3}$, $k = 5$).

when a 1 m length of packed capillary column is used. Therefore, efficiency should be sacrificed for speed of analysis. Most packed capillary SFC experiments are carried out at a mobile phase velocity of 1–10 cm s^{-1}, which is well in excess of the value required to produce the lowest plate height. This certainly causes a decrease in the number of plates; for a 1 m × 200 μm i.d. packed capillary column, at an average linear velocity of $u = 0.06$ cm s^{-1} $n = 46000$ and at $u = 1$ cm s^{-1} $n = 1000$. Therefore, the average linear velocity should be maintained as near to the optimum value of a Van Deemter plot as possible.

The most elegant way of developing a temperature programmed restrictor would be to find a series of correlations between the column flow rates and temperatures of the restrictor at various pressures. This was accomplished using the Alltech Model 7445 flow meter. The mobile phase flow velocities as a function of the temperature of the restrictor and the pressure of the column were measured using different lengths of 7 μm fused silica tubes as restrictors (Fig. 3). It is demonstrated that if the temperature of the 7 μm i.d. fused silica tubing is varied, the flow rate can be varied and can also be maintained near the optimum value of a Van Deemter curve.

In Fig. 3, it is seen that when the temperature of the restrictor is increased, the flow rates are rapidly decreased. This is explained theoretically by Poiseuille's equation. In this equation, for the compressible gas, the rate of flow is

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{16 \eta l}\left(\frac{p_i^2 - p_0^2}{p_m}\right) \tag{3}$$

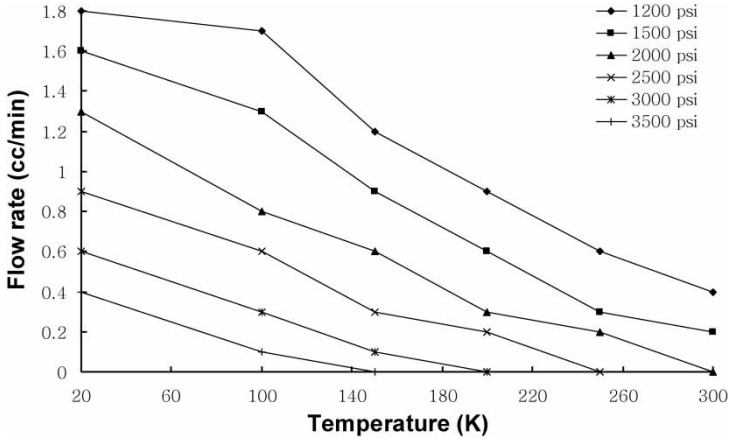

Figure 3. The flow rates as a function of temperature at various pressures of CO_2 using a 7 μm × 20 cm restrictor.

where P_i is the inlet pressure, P_0 is the outlet pressure, and P_m is the pressure at which the volume of the gas was measured. From Eq. (3), as the temperature of the restrictor is increased, the viscosity η of the fluid is decreased, resulting in increasing mass flow rate.

The mixtures of thirteen fatty acid methyl esters (13:0, 14:0, 15:0, 16:0, 17:0, 18:0, 18:1 n-9, 18:3 n-9, 18:3 n-12, 18:3 n-15, 19:0, 20:0, 21:0) were separated using a packed capillary SFC/UV system for evaluating the feasibility of the temperature controlled restrictor described above, while the separations performed pressure programming over a fairly wide range. The reason why a UV detector is used is that fatty acid methyl esters have an excellent UV absorbing functionality, and supercritical carbon dioxide fluid exhibits little background absorbance at 206 nm. Unlike the FID, which is a very nonspecific and destructive detector, the UV detector can provide compound specific information and it is highly sensitive. For this experiment, the UV detector was tuned to 206 nm, which is the characteristic absorption wavelength of fatty acid methyl esters. The flow through the temperature controlled restrictor can be controlled by varying the temperature of the restrictor. As the pressure programme advances, the restriction of the temperature controlled restrictor should be increased by increasing its temperature to keep the linear velocity of the mobile phase in the column constant.

As a control, we tried an SFC separation of thirteen fatty acid methyl esters without varying the temperature of the temperature controlled restrictor. Figure 4 shows the chromatogram obtained. In fact, the temperature controlled

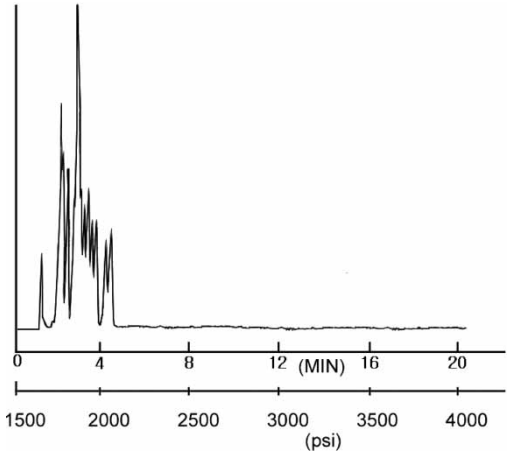

Figure 4. Supercritical fluid chromatograms of thirteen fatty acid methyl esters (13:0, 14:0, 15:0, 16:0, 17:0, 18:0, 18:1 n-9, 18:3 n-9, 18:3 n-12, 18:3 n-15, 19:0, 20:0, 21:0) without controlling the temperature of the temperature controlled restrictor.

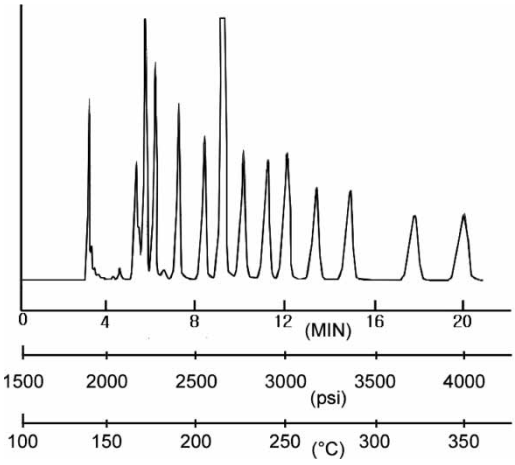

Figure 5. Supercritical fluid chromatograms of thirteen fatty acid methyl esters (13:0, 14:0, 15:0, 16:0, 17:0, 18:0, 18:1 n-9, 18:3 n-9, 18:3 n-12, 18:3 n-15, 19:0, 20:0, 21:0) with controlling the temperature of the temperature controlled restrictor.

restrictor was kept at room temperature, but the experiment was performed with pressure programming. The initial pressure was 1,500 psi, increased at 125 psi min^{-1} to the final pressure of 4,000 psi.

Subsequently, when the temperature controlled restrictor was tried, the resolution of the chromatogram was increased (Fig. 5). The temperature of the temperature controlled restrictor was varied from 100 to 350°C to maintain the flow rate as low as possible. The packed capillary column used was only 1 m long to avoid a long analysis time. The better resolution in Fig. 5 is because a low average linear velocity was maintained by the use of the temperature controlled restrictor.

In conclusion, at present most packed capillary supercritical fluid chromatograms are obtained at a linear velocity that is much higher than the optimum value on the Van Deemter curve. With pressure programming, the linear velocity increases still further, causing a decrease in efficiency. We have developed a temperature controlled restrictor for the SFC/UV system that can be programmed to increase the restriction during a pressure programmed run, in order that the linear velocity remains constant and the chromatographic efficiency increases.

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