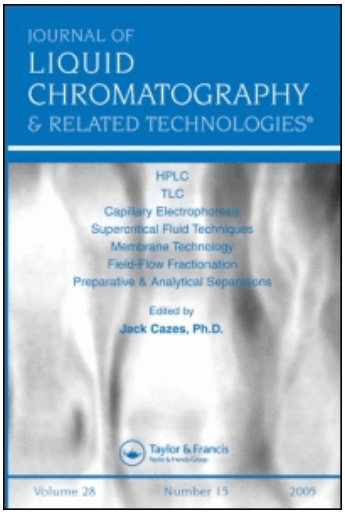

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SUPERCRITICAL FLUID CHROMATOGRAPHIC DETECTION BY USE OF A PARALLEL FLOW RESTRICTOR

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ABSTRACT

In supercritical fluid chromatography (SFC), the role of the flow restrictor is not only to maintain supercritical conditions throughout the column but also to provide the necessary interface between the column and the detector. In the previous paper,[1] a new type of flow restrictor called parallel flow restrictor was introduced. At that time, the parallel flow restrictor was used only for the flow control. In this paper, the parallel flow restrictor was used not only for the flow control but also for the interface to the second detector. A supercritical fluid chromatographic system with a combination of two detectors based on physically different principles, flame ionization and UV absorption, was used.

INTRODUCTION

Klesper et al.[2] first reported the use of a supercritical fluid as a chromatographic mobile phase in 1962. Although the work of this group[2,3] and later that of Giddings and co-workers[4,5] and Sie and Rijnders[6,7], with both dense gases and supercritical fluids, helped to develop supercritical fluid chromatography (SFC) both experimentally and theoretically, the technique did not become popular until some 20 years later.

In 1981, a re-emergence of the technique was initiated following a report by Novotny et al.[8] describing separations performed using open-tubular capillary columns and supercritical pentane as the mobile phase. Since then, hundreds of papers have appeared describing SFC instrumentation, coupling of SFC with various detectors, and numerous applications of the technique.

In SFC, various types of detectors including the UV absorption detector,[9] flame ionization detector (FID),[10] fluorescence,[11] refractive index,[12] mass spectrometer,[13] etc., have been used. With supercritical CO_2 and several other SFC mobile phases, it is possible to use a FID. This provides the ideal combination of a solvating mobile phase and sensitive and universal detection. With GC, both volatility and thermal stability are required for a successful analysis. Although these are not required for HPLC, sensitive, universal detection is very difficult today with liquid mobile phases. The combination of SFC and FID is certainly a convenient sensitive capability for determining low volatility or thermally labile analytes that do not strongly absorb light. For these reasons, FID is the most popular detector in capillary SFC. UV detectors have been the most preferred in packed column SFC.[14]

For fractionation, 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 190nm, 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 50-100 μm i.d. open-tubular SFC columns with gas chromatography (GC)-type detectors such as the flame-ionization detector, the role of the flow restrictors is not only to maintain supercritical conditions

throughout the column but also to provide the necessary sample introduction interface between the column and the detector. Three types of flow restrictors are frequently used in capillary SFC: linear restrictors,[15] tapered restrictors,[16] and integral restrictors.[17]

Recently, we developed two different types of temperature programmable restrictors, i.e., a two-stage restrictor[18] and a parallel flow restrictor.[1] Among them, a parallel flow restrictor consists of two separate restrictors in parallel. In this paper, the successful coupling of capillary SFC to both flame ionization (FID) and UV absorption detection by use of a parallel flow restrictor is described.

Recently, there has been a good deal of new interest in SFC using packed capillary columns.[19] Advantages of packed column SFC include fast analysis speeds, great sample capacities, and high plate numbers per unit length. Advantages of open tubular column in SFC include small pressure drop per unit column length which allows the use of long column to generate high efficiencies for the separation of complex mixtures. It was known that packed capillary columns can take advantages of both colunm types, i.e., packed and capillary.[20]

Due to these many anvantages, packed capillary columns have been used extensively in this work. For the present work, we used a fused silica capillary column (dimensions: 200μm i.d. × 60cm) packed with 5μm ODS particles.

EXPERIMENTAL

The chromatographic system comprised a Model 600 SFC pump (Dionex, Sunnyvale, CA, USA) for pressure control of the carbon dioxide mobile phase and the Model 600 GC / SFC oven (Dionex). The column used was a 60cm × 200μm i.d. fused silica capillary packed with 5μm ODS bonded silica.[19] The packing material was obtained from Phenomenex (Rancho, Palos Verdes, CA, USA). The packed capillary column was connected directly to the injection valve, and the UV detection of solute occurred immediately after the bed support using the 200μm i.d. column as the flow cell. A model 203 UV/ Vis detector (Linear, Reno, NV, USA) was used for UV detection.

The system was equipped with a C14W loop injector (valco Instruments, Houston, TX, USA) and a flame ionization detector. SFC grade carbon dioxide (Scott Specialty Gases, Plumstcadville, PA, USA) was used as the mobile phase.

The effluent from the column was split between the flame ionization detector and UV absorption detector with the parrallel flow restrictor. The splitter was a Valco 1/16 union in which the column was connected to one end and the FID and UVD to the other end. The parallel flow restrictor is comprised of two linear restrictors (14μm i.d. × 10cm).

Flow rates were measured using an Alltech Flowmeter (7445). This flowmeter monitors the mass flow rate of the gas in the range of 0 ~ 50 standard cubic centimeters per minute (SCCM). Accuracy is 20% of full scale over a wide temperature and pressure range, and time response is 2 seconds.

RESULTS AND DISCUSSION

In the previous paper,[1] we found a series of correlations between the column flow rates and temperatures of the restrictor at various pressures to develop a temperature programmed restrictor. 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 length of 14μm fused silica tubes as restrictors. It was also demonstrated that if the temperature and the length of the 14μm i.d. fused silica tubing is varied, the flow rate could be varied, and could also be maintained near the optimum value of a Van Deemter curve. For example, it was seen that when the temperature of the restrictor was increased, the flow rates were decreased to a noticeable extent. It was also seen that if the length of the restrictor was doubled, the flow rates were halved.

These phenomena can be explained theoretically by Poiseuille's equation. In this equation, for an incompressible fluid, the volume of flow(ΔV) through a tube (radius r, length l, viscosity η) in some time interval(Δt) is:

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4 \Delta P}{8 \eta l} \qquad (1)$$

where ΔP is the pressure drop between the ends. If the fluid is a compressible ideal gas, the rate of flow is

$$\frac{\Delta V}{\Delta t} = \frac{\pi r^4}{16 \eta l}\left(\frac{P_i^2 - P_o^2}{P_m}\right) \qquad (2)$$

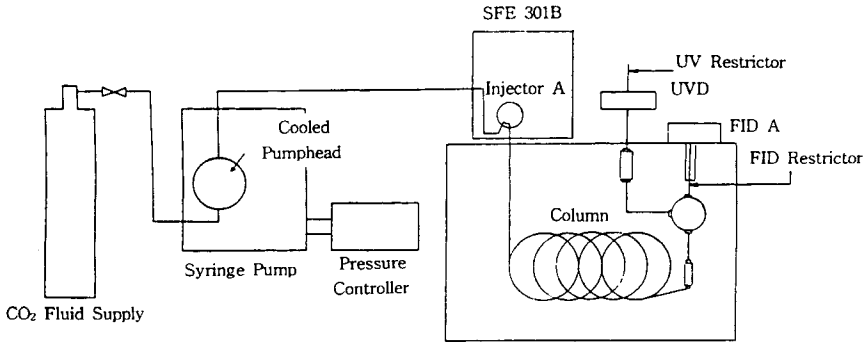

Figure 1. Schematic diagram of the parallel flow restrictor.

where P_i is the inlet pressure, P_o is the outlet pressure, and P_m is the pressure at which the volume of the gas was measured. As a supercritical fluid is not a gas and not a liquid, it is difficult to apply one of these equations to SFC restrictors, but as far as the viscosity and the length are concerned, both of these equations agree that the mass flow rate through the tube is inversely proportional to the viscosity of the fluid and the length of the tube. It is obvious that when the temperature of the tube is increased, the viscosity of the fluid passing through it also increases. For these reasons, in SFC, as the temperature of the restrictor is increased, the flow rate is decreased.

In this paper, the successful coupling of packed capillary SFC to both flame ionization (FID) and UV absorption detection by use of a parallel flow restrictor is described. Since a parallel flow restrictor consists of two linear restrictors in parallel, it is not difficult to install two detectors in parallel on a column of supercritical fluid chromatographic system(see Figure 1).

Figure 2 and 3 show chromatograms of four polyaromatic hydrocabons detected by both FID and UVD. As expected, the relative ratio of flame ionization detector response and UV absorption detector response was dependent on the temperatures of two restrictors. Individual compounds also showed different detector responses. Anthracene and Chrysene showed much greater detector response than FID, Pyrene showed similar detector responses for both FID and UV. First of all, the temperature of a restrictor connected to FID(it will be called FID restrictor afterwards) was maintained at 320°C, and the temperature of a restrictor connected to UV detector was varied from 50°C to 200°C. The relative detector response ratios for Pyrene were obtained and

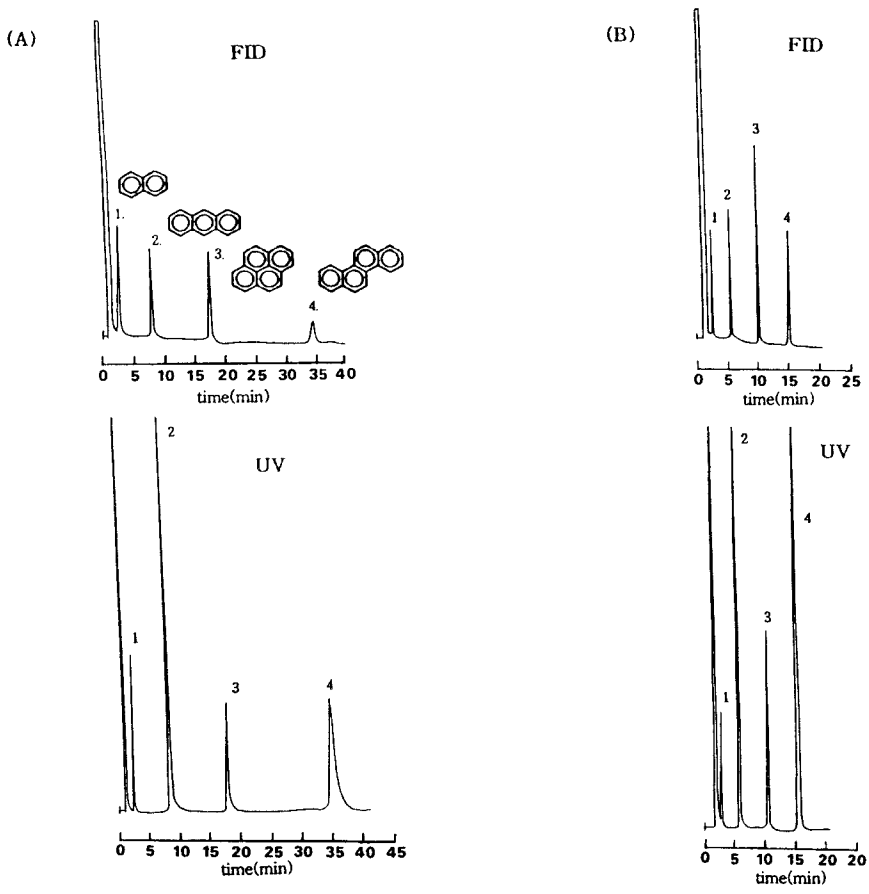

Figure 2. Supercritical fluid chromatograms of mixture of polyaromatic hydrocarbons at the UV restrictor temperature of (A) 150°C and (B) 60°C conditions: 60 cm × 200 μm i.d. fused silica capillary packed column, 5μm ODS silica, CO_2 mobile phase at 100°C; pressure programmed.

shown in Table 1. Figure 2 shows the supercritical fluid chromatograms of mixture of polyaromatic hydrocarbons at different UV restrictor temperatures maintaining the temperature of FID restrictor at 320°C. As the temperature of the restrictor connected to UV detector increases, the relative detector response (FID signal / UV signal) decreases.

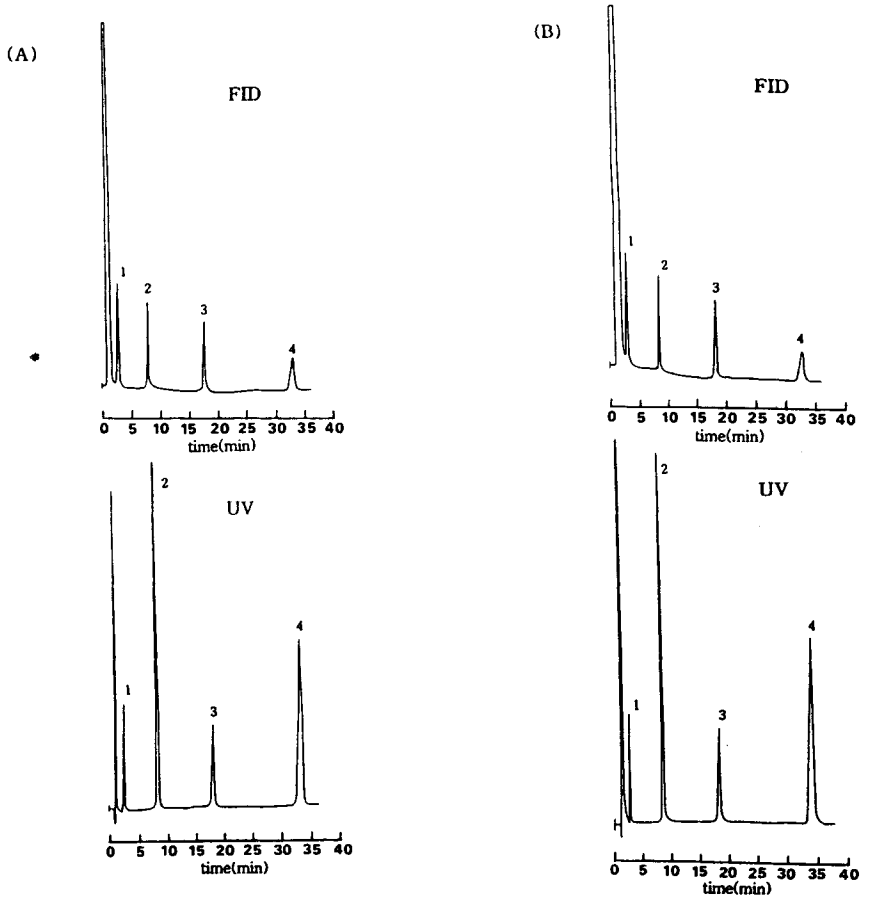

Figure 3. Supercritical fluid chromatograms of mixtures of polyaromatic hydrocarbons at the FID.

This phenomena, the decrease of the UV detector signal with increasing the temperature of the restrictor connected to UV detector, can be understood that, as the temperature of the restrictor increases, the volume of the fluid passing through it also increases, changing the extent of restriction of the restrictor connected to UV detector.

Other experiments, in which the temperature of the UV restrictor is maintained at 100°C, the temperature of the FID restrictor is varied, have been made.

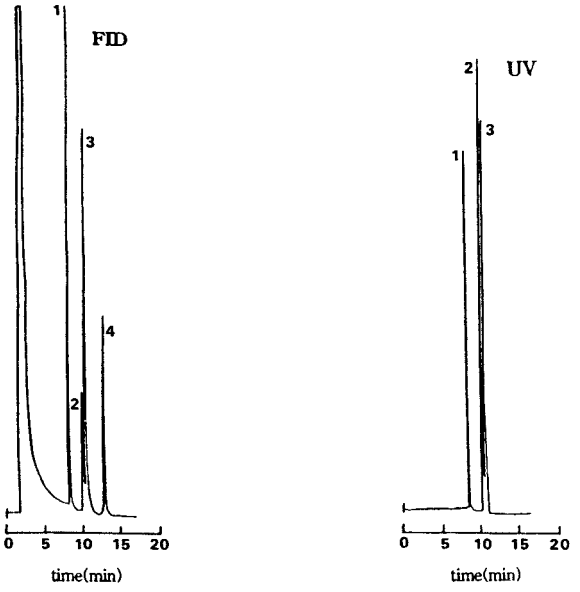

Figure 4. Supercritical fluid chromatograms of mixture of pesticides conditions: 60 cm × 200 μm i.d. fused silica capillary packed column, 5μm ODS silica, CO_2 mobile phase at 100°C; pressure programmed from 100atm to 300 atm at 4atm/min., FID restrictor temperature at 300°C, UV restrictor temperasture at 100°C, 280nm UV detection. Peak identification: 1. Carbofuran 2. Chlorpyrifos 3. Naphthol 4. Lindane.

Table 1

The Relative Ratios of FID Signal and UVD Signal at Different UV Restrictor Temperatures Maintaining the Temperatures of FID Restrictor at 320°C

Temp. of UV Restrictor	FID Signal / UVD Signal
50°C	2.02
100°C	1.78
150°C	1.53
200°C	1.42

Table 2

The Relative Ratios of FID Signal and UVD Signal at Different UV Restrictor Temperatures Maintaining the Temperatures of FID Restrictor at 100°C

Temp. of UV Restrictor	FID Signal / UVD Signal
360°C	0.174
340°C	0.171
320°C	0.175
280°C	0.173

The relative ratios of FID signal and UVD signal were obtained (Table 2). Figure 3 shows the chromatograms when the temperature of FID restrictor was varied from 360° to 320° maintaining the temperature of UVD restrictor at 100°C, the relative detector response ratios for Pyrene were almost same. It is well known that when the temperature of FID block is increased, the FID detector response is also increased. In this case, this effect was compensated for the decreasing of FID signal owing to the elevation of the temperature of FID restrictor.

Finally, two detectors in parallel with parallel flow restrictors were used for the SFC separations of pesticides. Figure 4 shows the chromatograms of mixtures of three pesticides using two detectors, i.e. FID and UVD and two restrictors. The temperatures of FID restrictor and UVD restrictor were 300°C and 100°C each. Although carbofuran, chlorpyrifos, and naphthol were detected by both detectors, lindane was detected only by FID.

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