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SPLITTING CONTROL AND SOLVENT EFFECTS IN SUPERCRITICAL-FLUID CHROMATOGRAPHY WITH FUSED-SILICA CAPILLARY COLUMNS

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SUMMARY

A computer-controlled splitting device was used to study splitting ratios from 1:3 to 1:500 in supercritical-fluid chromatography. At low to medium-high splitting ratios, a solvent effect, dependent on the solvent density, was observed. Chromatographic data obtained for two test mixtures (polynuclear aromatic hydrocarbons and *n*-alkanes) are comparable to those in the literature.

INTRODUCTION

Supercritical-fluid chromatography (SFC), especially capillary-column SFC, suffers from many of the problems inherent in capillary-column gas chromatography (GC). One area of SFC research is the (reproducible) injection of the sample into the capillary column. Owing to transport phenomena and diffusion effects in the supercritical fluid, capillary columns have inner diameters of 100 μm or less. In order to achieve a good separation and to avoid column overloading, the injected sample is split, and only a portion is loaded on to the column. This loss of detectable analyte consequently limits applications in trace analysis.

Under SFC conditions, the retention times of analytes are much higher than those in GC owing to the much higher density of the eluent inside the column and the limited flow through the column restrictor. The use of shorter capillary columns (2–10 m) reduces the retention times of analytes and the residence times of solvents, but the column efficiency is also reduced. With short and very narrow columns, the injection volume becomes very important. A simple calculation shows that a 1-μl plug injected into a 100-μm diameter column would result in a 127-mm long plug inside the column. A 60-nl plug still results in a length of 7.6 mm, which is much longer than 1 HETP in capillary SFC. In other words, a 7.6-mm plate height in a 2-m long capillary column would yield only 263 theoretical plates; a 127-mm plate height gives 15.7

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theoretical plates. As the flow-rates are usually much higher than the optimum value, the chromatogram becomes very poor.

Much effort has been expended on overcoming such injection problems. A constant splitting device is currently the most common approach in capillary SFC. Unfortunately, the splitting changes with any change in the experimental conditions, *e.g.*, pressure and temperature[1], and there are many problems in quantitative applications[2]. Instead of a split-injection technique, direct injection or time-controlled direct injection is now more often used[2]. This allows better reproducibility of injection and the amount injected can therefore be more easily optimized for efficient chromatography.

We have taken a new approach to split injection in SFC. A controller has been developed that can be used on injection valves with different internal or external sample-loop volumes. It can also be time-programmed in order to save supercritical fluid. Preliminary results are reported.

EXPERIMENTAL

The SFC system was made in-house (Fig. 1, bottom) and consisted of a heated carbon dioxide cylinder, which gave pressures of up to 20.0 MPa (*ca.* 200 atm), with either a 0.2-μl or (in most instances) a 2-μl Valco C14W injection valve (Valco, Houston, TX, U.S.A.)[3]. The splitting system was similar to those described elsewhere[4], with the exception that the split outlet was connected to a Nupro type SS2-A needle valve (BEST. Ventil + Fitting, Dortmund, F.R.G.), which was driven by a stepping motor. The stepping motor was controlled via a two-point control program of a CBM 64 (Commodore) personal computer. A simple schematic diagram explains the split control system (Fig. 1, top). The disturbance $e(t)$ is the difference between the reference input x_w (keyboard value) and the actuating signal $y(t)$ (pressure gauge value). The manipulated variable $U(t)$ adjusts the disturbance to small values; in the apparatus this means control of the direction of the stepping motor and the period of motor action. The software was written in-house. The split-outlet system and the software can easily be modified for column pressure and density control under SFC conditions; this will be reported in a subsequent paper.

The flow diagram of the two-point controller is shown in Fig. 2. The hysteresis becomes important if rapid changes are required, as every change requires (motor run) time. Once the deviation between $y(t)$ and x_w has been determined, the control program is set for no changes ("Yes"), open valve or close valve.

The columns used were either a 10 m × 100 μm I.D. BP-1 or 12 m × 100 μm I.D. BP-10 fused-silica capillary column (Scientific Glass Engineering, Weiterstadt, F.R.G.). The column was kept inside a Carlo Erba Fractovap HRGC 4160 instrument (Erba Science, Hofheim/Taunus, F.R.G.). The column end restrictor was a 90-mm length of 10 μm I.D. fused-silica capillary, connected with a butt connector and inserted into a flame ionization detector (FID) which was kept at 300°C.

Two samples were used: one contained a mixture of three polycyclic aromatic hydrocarbons (PAHs) (naphthalene, biphenyl and phenanthrene) dissolved in various solvents and the other contained six *n*-alkanes (C_{12}–C_{16} and C_{18}).

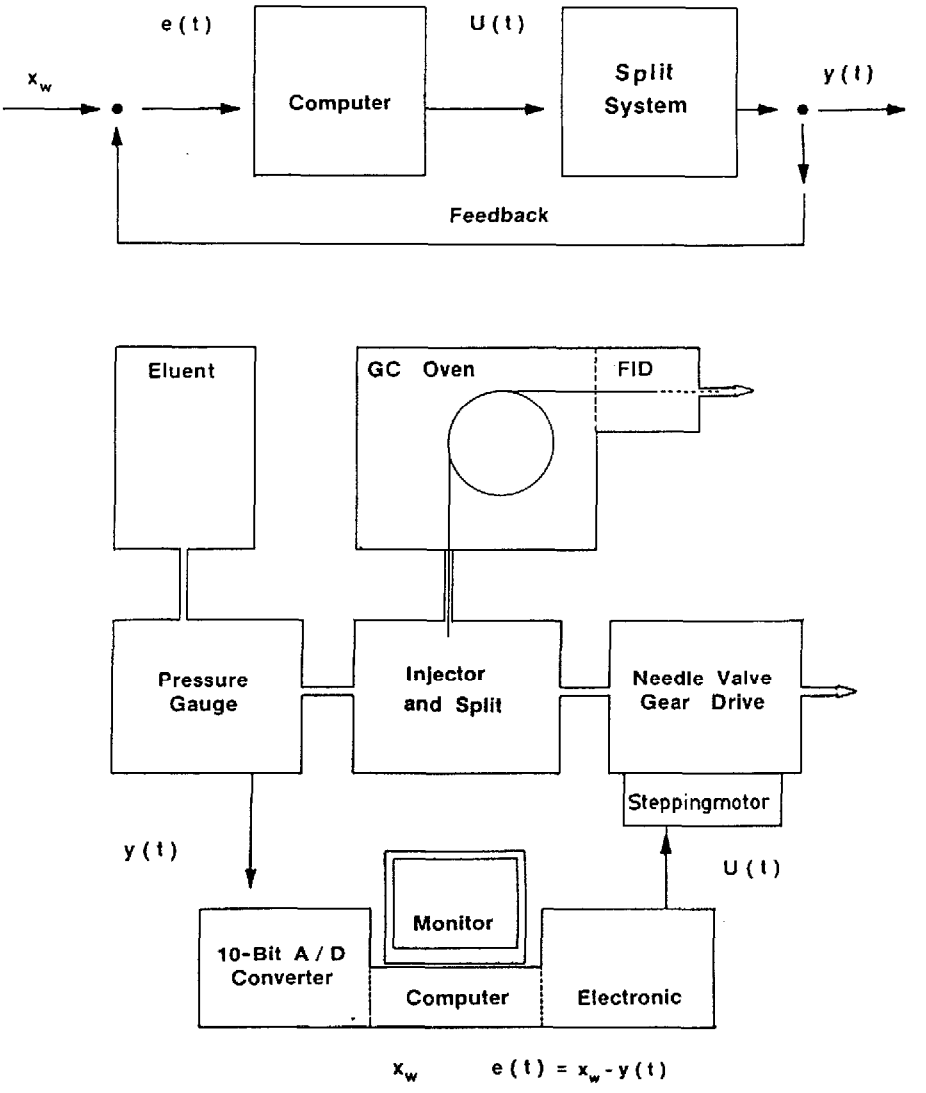

Fig. 1. Schematic diagrams of (top) theoretical control system and (bottom) SFC apparatus and computer control system. A/D = Analog-to-digital.

RESULTS AND DISCUSSION

During an experiment the SFC system was maintained at constant pressure, but for different experiments the pressure was varied by changing the temperature of the carbon dioxide cylinder. The pressure was monitored with a pressure gauge to provide $y(t)$ so that the splitting ratios were kept constant. The reference (input) value (x_w) was compared with $y(t)$ five times per second, which allowed a rapid response for the needle valve positioning. First, the splitting control was used to determine the

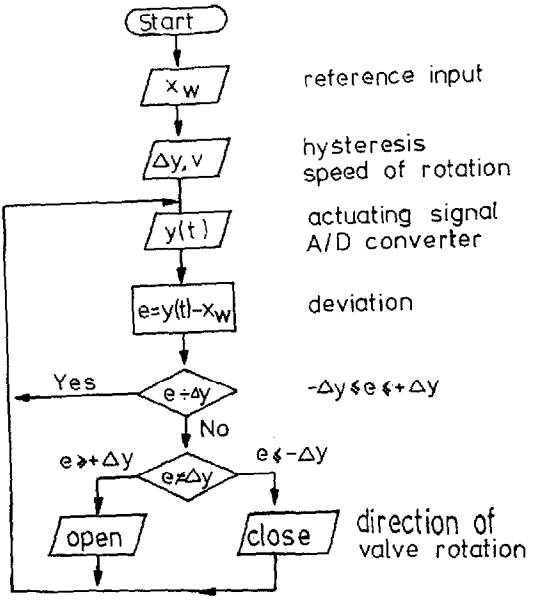

Fig. 2. Flow diagram of the two-point controller. Parallelograms, computer input/output symbol; rectangle, computer calculation symbol; diamonds, computer decision step symbol.

capacity factors (k') of both test mixtures. They were in agreement with data reported in the literature[5]. A slight change in retention times (t_r) at different splitting ratios was observed (Fig. 3). The column outflow remained constant at all times.

A dependence on splitting ratio and sample solvent density was unexpected. At a low splitting ratio (1:3), the retention times of the PAHs increased with increasing

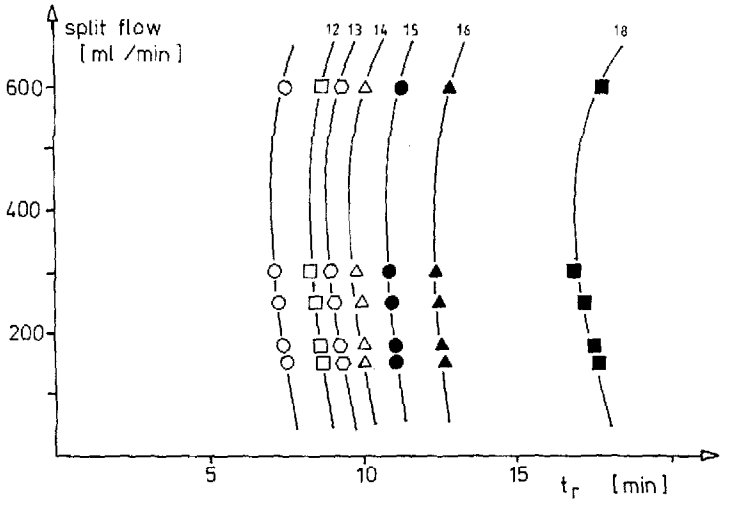

Fig. 3. Dependence of retention time on splitting ratio for six *n*-alkanes (C_{12}–C_{18}, identified by the numbers above the lines) in *n*-heptane (○). Column outflow into detector: 2.1 ml/min.

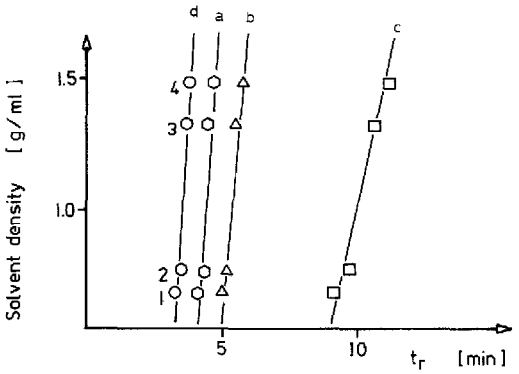

Fig. 4. Effect of solvent density on retention time: a = naphtalene; b = biphenyl; c = phenanthrene; d = solvent (1 = *n*-heptane; 2 = cyclohexane; 3 = dichloromethane; 4 = trichloromethane). Splitting ratio, 1:3; temperature, 85°C; pressure, 11.0 MPa (*ca.* 110 atm).

density of the solvent (Fig. 4). At a high splitting ratio (1:350), the retention times remained constant for every solvent. This could be explained by modification of the column surface at the column head due to the solvent[6] and/or a change in the splitting ratio due to changed flow characteristics in the splitting restrictor. With increasing splitting ratios (up to 1:100), this effect becomes less obvious, but is still apparent. As the concentration was the same in all instances, a solubility effect can be excluded. A solvent and/or density effect is, therefore, more likely than a flow effect. All of these experiments were performed under isodensic conditions, and phenanthrene was eluted with a leading peak, which accounts for its different slope in Fig. 4. From the preliminary experiments is can be concluded that: (1) variable splitting control is one alternative to constant splitting in SFC; (2) large splitting ratios are one alternative to time-controlled injection; and (3) at low splitting ratios a solvent and/or density effect is observed.

In the future, further evaluation of the system and more data are needed to confirm its general applicability. The use of the computer-controlled splitting valve allows much greater and more easily adjustable ranges of splitting ratio, which, as our current data show, can be easily reproduced. In addition, splitting control might also be useful in GC applications.

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