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CAPILLARY SUPERCRITICAL-FLUID CHROMATOGRAPHY WITH CONVENTIONAL FLAME DETECTORS

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SUMMARY

Coupling of a supercritical-fluid chromatograph to flame-ionization and nitrogen-thermionic detectors is described. A fused-silica capillary restrictor was used to maintain pressure in the analytical column and to expand the effluent into the detector flame jet. Selected applications demonstrate the usefulness of these gas chromatographic detectors in supercritical-fluid chromatography.

INTRODUCTION

Although supercritical-fluid chromatography (SFC) was first demonstrated over twenty years ago[1], it has experienced rather slow growth and limited acceptance as a useful analytical technique. This is principally a result of the technological difficulties encountered in handling supercritical fluids in chromatographic systems. Solvent pumps, sample introduction systems and detectors require modifications and design improvements in order to operate properly. Furthermore, stable analytical columns containing immobilized stationary phases are needed.

The rapid growth of high-performance liquid chromatography (HPLC) has provided many of the technological solutions to SFC. High-pressure pumps and injection systems, and bonded-phase columns are now available. Instrumentation for both packed column and capillary column SFC has been described[2–6].

As is also the case in HPLC, detection is the major instrumental problem in SFC. The liquid chromatographic detectors that have been employed for SFC include the UV-absorption[2–4,7], fluorescence[5], refractive-index[8], adsorption[9] and scintillation[7] detectors. The UV-absorption detector has been the most popular detector because most SFC mobile phases are transparent in the UV region, and most of the high-molecular-weight compounds usually investigated contain one or more chromophores.

The only gas chromatographic (GC) detectors that have been employed for SFC are the flame-ionization[4,10–14] and thermoconductivity[13] detectors. The many desirable characteristics of the flame-ionization detector in GC can be realized in SFC when mobile phases, such as CO_2, N_2O and NH_3 are used. The main problem with this detector is encountered because the mobile phase must be decompressed before detection. It was found[1,12] that when the supercritical fluid was decompressed

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at the exit of the chromatographic column, relatively involatile solute molecules reached a state of extreme thermodynamic instability, and immediate molecular association and wall condensation occurred. This resulted in line clogging and spiked peaks. The spikes were attributed to single fog particles that enter the detector and create short ion bursts. This behavior was intensified when large samples were analyzed.

Both UV-absorption and fluorescence detectors have been used with capillary SFC[5,6,15]. In addition, a capillary supercritical-fluid chromatograph has been interfaced to a mass spectrometer[16,17]. In this paper, the successful coupling of capillary SFC to both flame-ionization (FID) and nitrogen-thermionic detection is described.

EXPERIMENTAL

The chromatographic system consisted of a Perkin-Elmer 601 liquid chromatograph syringe pump, a Hewlett-Packard 5700 gas chromatograph oven with conventional FID and nitrogen–phosphorous detection (NPD), and an Apple II+ microcomputer. The supercritical fluid (CO_2 or N_2O) was delivered by the syringe pump to a 50- or 75-μm I.D. fused-silica (Hewlett-Packard, avondale, PA, U.S.A.) column, which was housed in the chromatograph oven. The column was prepared by statically

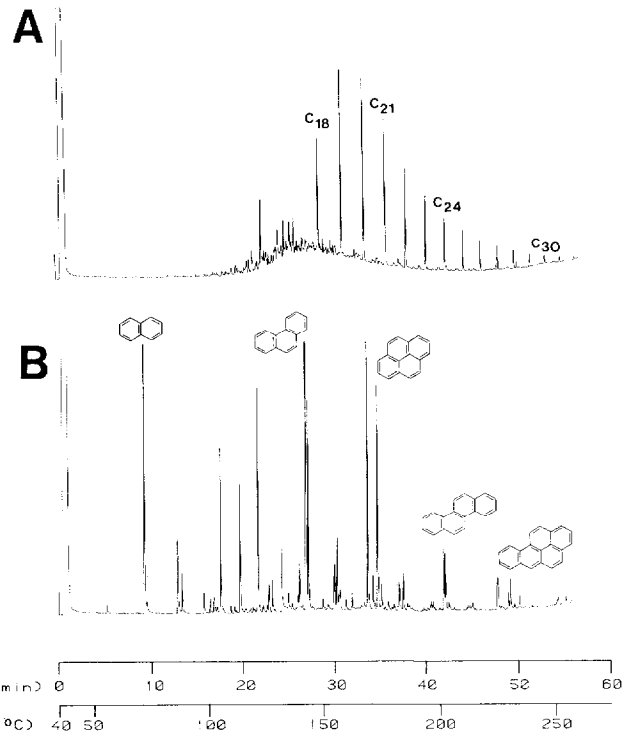

Fig. 1. Gas chromatograms of (A) an aliphatic fraction of a solvent-refined coal and (B) a coal tar. Conditions: 20 m × 300 μm I.D. fused-silica column, SE-54 stationary phase (0.25-μm film thickness) cross-linked with azo-*tert.*-butane; temperature programmed from 40°C to 265°C at 4°C min^{-1} after an initial 4-min isothermal period; hydrogen carrier gas.

coating a 0.25-μm film of SE-54 (in *n*-pentane) on the column wall and cross-linking with azo-*tert.*-butane[18]. Samples to be analyzed were introduced into the capillary column with a 0.2-μl internal sample volume Valco valve (at room temperature) in conjunction with an inlet splitter[5]. Pressure restriction and connection to the flame detectors was accomplished by connecting 9 cm × 10 μm I.D. fused-silica capillary tubing to the column end by means of a Valco butt-connector. The end of the restrictor was inserted into the detector base, through a 300-μm I.D. capillary sleeve, and positioned approximately 2 cm below the tip of the flame jet. The oven temperature was held constant at 40°C for CO_2 and 46°C for N_2O, and the detector temperature was usually maintained at approximately 350°C.

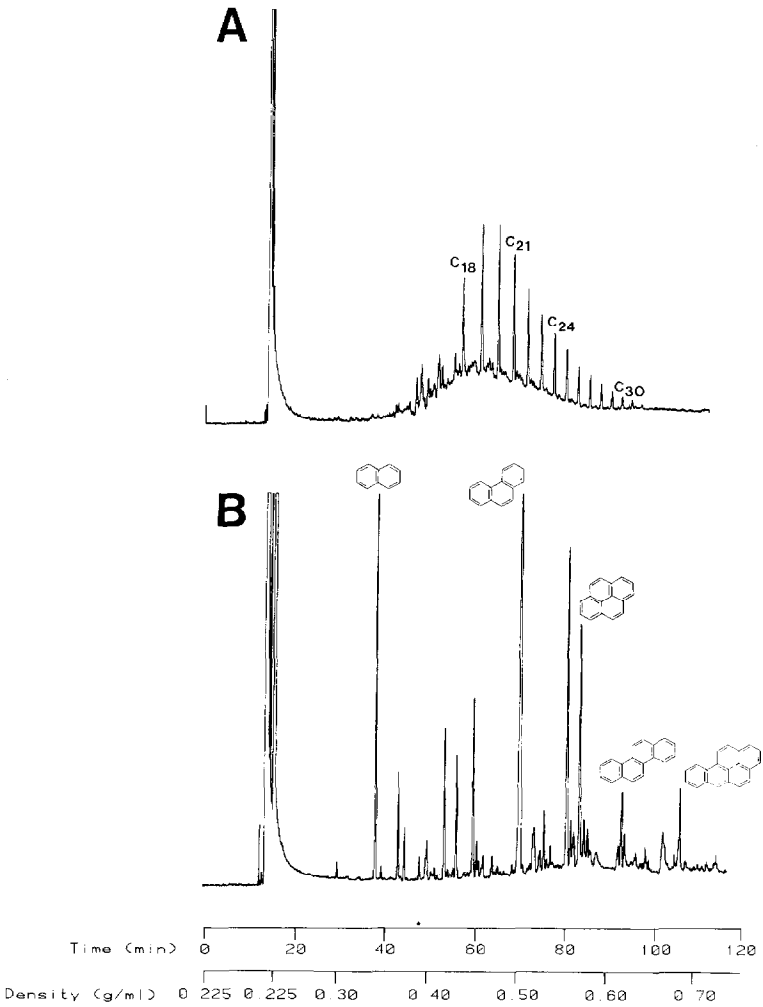

Fig. 2. Supercritical-fluid chromatograms of (A) an aliphatic fraction of a solvent-refined coal and (B) a coal tar. Conditions: 34 m × 50 μm I.D. fused-silica column, SE-54 stationary phase (0.25-μm film thickness) cross-linked with azo-*tert.*-butane; CO_2 mobile phase at 40°C; density programmed from 0.225 g ml^{-1} to 0.70 g ml^{-1} at 0.005 g ml^{-1} min^{-1} after an initial 15-min isoconfertic (constant density) period.

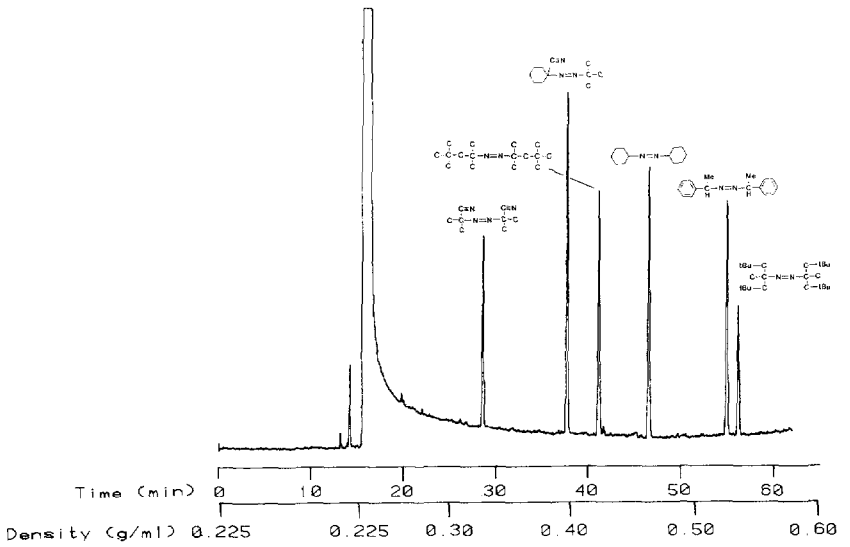

Fig. 3. Supercritical-fluid chromatogram of azo compounds. Conditions as in Fig. 2, except density programmed from 0.225 g ml^{-1} to 0.575 g ml^{-1} at 0.0075 g ml^{-1} min^{-1} after an initial 15-min isoconfertic period.

RESULTS AND DISCUSSION

Figs. 1 and 2 show chromatograms of two coal products (an aliphatic fraction of a solvent-refined coal and a coal tar) analyzed by both capillary GC and SFC. As can be seen, capillary SFC has a resolving power remarkably similar to GC when longer analysis times are allowed. Density programming of CO_2 produces an elution

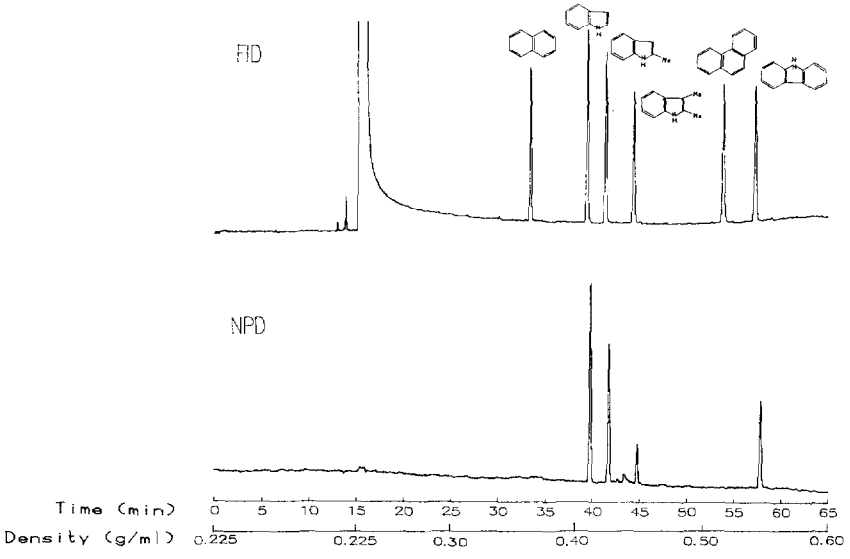

Fig. 4. Supercritical-fluid chromatogram of two polycyclic aromatic hydrocarbons and four nitrogen heterocycles. Conditions as in Fig. 2, except density programmed from 0.225 g ml^{-1} to 0.60 g ml^{-1} at 0.0075 g ml^{-1} min^{-1} after an initial 15-min isoconfertic period.

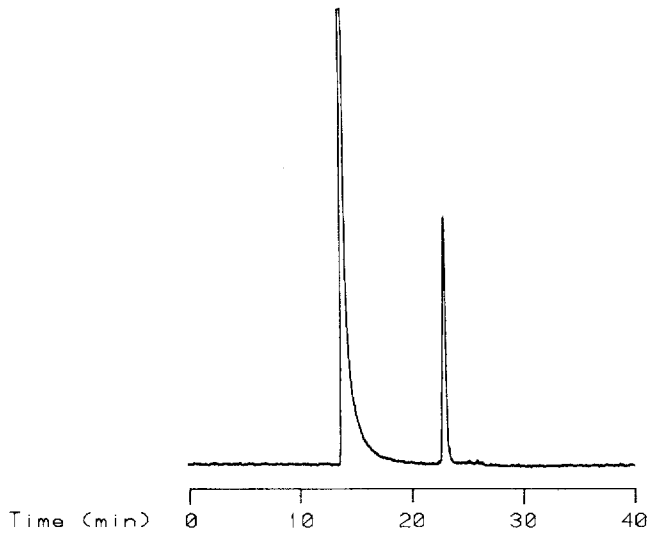

Fig. 5. Supercritical-fluid chromatogram of cholesterol. Conditions: 14 m × 0.75 μm I.D. fused-silica column, SE-54 stationary phase (0.25-μm film thickness) cross-linked with azo-*tert.*-butane; N_2O mobile phase at 46°C; isoconfertic at 0.562 g ml^{-1}.

order (selectivity) very similar to GC. However, C_{30} is eluted before benzo[*a*]pyrene in SFC, while the reverse is true in GC. This is due to the solvating power of the supercritical fluid (*i.e.*, the low-polarity CO_2 preferentially solvates and elutes the non-polar C_{30} before the less soluble polycyclic aromatic hydrocarbon).

A mixture of azo compounds was analyzed by capillary SFC to demonstrate the application to thermally labile compounds (Fig. 3). Good separation of all six compounds was achieved by density programming the CO_2 mobile phase at a rate of 0.0075 g ml^{-1} min^{-1}, resulting in an analysis time of less than 60 min.

To evaluate the use of a thermionic detector, the flame ionization detector collector was replaced with a nitrogen–phosphorus detector collector, approximately 30 ml min^{-1} helium make-up gas was added through the flame jet and a proper bead current was applied. Fig. 4 shows the results of the analysis of a standard mixture, containing two polycyclic aromatic hydrocarbons and four nitrogen heterocycles. The nitrogen–phosphorus detector performed as trouble-free for SFC as for GC, giving good selectivity of nitrogen-containing compounds over hydrocarbons. The nitrogen–phosphorus detector was also evaluated with N_2O as the carrier fluid. Again, good selectivity was observed, but in this case the solvent gave a positive recorder deflection, then fell below baseline, followed by a positive deflection which returned to baseline. The remainder of the chromatogram was normal. This indicates that when N_2O is used as the mobile phase, the detector selectivity is lower. This observation is presently under further study.

Nitrous oxide was found to possess some polar character, as indicated by its ability to elute underivatized cholesterol at 46°C (Fig. 5). On this relatively short (14 m) 75-μm I.D. column, cholesterol was eluted at 0.562 g ml^{-1} with a capacity factor (k') < 1). Nitrous oxide has been used in density programming to a density of 0.76 g ml^{-1}, indicating the potential for analysis of other, more polar compounds without the need for derivatization.

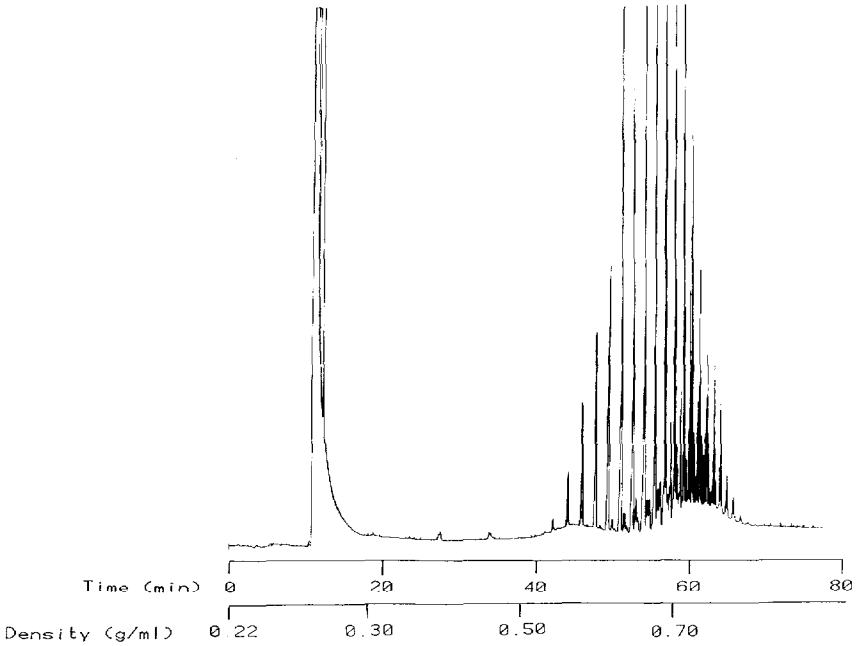

Fig. 6. Supercritical-fluid chromatogram of paraffin wax. Conditions: 20 m × 50-μm I.D. fused-silica column, SE-54 stationary phase (0.25-μm film thickness) cross-linked with azo-*tert.*-butane; CO_2 mobile phase at 40°C; density programmed from 0.22 g ml^{-1} to 0.76 g ml^{-1} at 0.01 g ml^{-1} min^{-1} after an initial 10-min isoconfertic period.

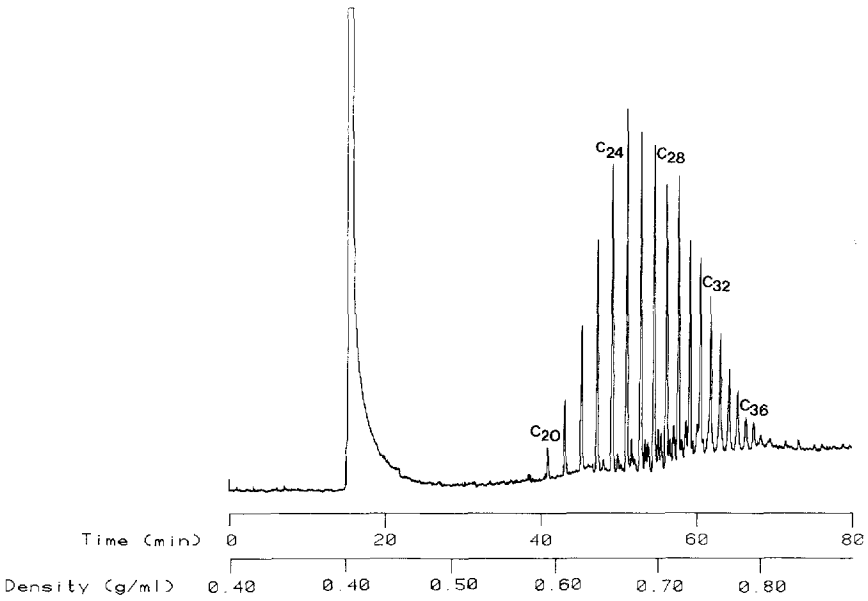

Fig. 7. Supercritical-fluid chromatogram of paraffin wax. Conditions as in Fig. 2, except density programmed from 0.40 g ml^{-1} to 0.80 g ml^{-1} at 0.0075 g ml^{-1} min^{-1}, after an initial 15-min isoconfertic period.

Finally, in addressing the problem of cluster formation during carrier fluid decompression, a paraffin wax, containing *n*-alkanes extending beyond C_{36}, was analyzed on a 20 m × 50 μm I.D. column, coated with SE-54. The chromatogram was recorded directly on a strip chart recorder (Fig. 6). As can be observed from the chromatogram, a definite spiking problem occurs with elution of *n*-alkanes as small as C_{24}. It was noted that the spiking consisted, for the most part, of very fast transients, which were much faster than the incline and fall of the peak itself. Furthermore, it was observed that even though spiking occurred during the elution of the chromatographic peak, no peak distortion (tailing) due to adsorption of clustered molecules in the restrictor was observed. By electronically filtering the higher-frequency component of the detector signal, the major portion of this spiking was eliminated. Good results were obtained when a time constant of approximately 1.5 sec was used in the low-pass filter (Fig. 7). The low-pass filter also amplified the 1-mV detector signal to 1 V in order to allow for data acquisition by a microcomputer; the acquisition rate was normally two samples sec^{-1}, and the acquired data were stored on a floppy disk for chromatogram reconstruction. With the exception of the paraffin analysis that was directly plotted by the strip chart recorder, all chromatograms shown were filtered with the low-pass filter.

It should be mentioned that other measures should be taken to reduce the clustering phenomenon. Smaller amounts of sample seem to cause less problem. With the use of 50-μm I.D. capillaries, small sample loads are already necessary to prevent overloading of the column. Other solutions to this problem are presently under study.

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