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SUPERCRITICAL FLUID CHROMATOGRAPHY AND SUPERCRITICAL FLUID CHROMATOGRAPHY-MASS SPECTROMETRY OF MARINE DIESEL FUEL

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SUMMARY

The application of capillary column supercritical fluid chromatography (SFC) and supercritical fluid chromatography-mass spectrometry (SFC-MS) to the analysis of the polycyclic aromatic hydrocarbon fraction of selected marine diesel fuel samples is described. The chromatographic separation methods utilized pressure or density programming techniques and small diameter (50 μm) capillary columns. This work demonstrates the feasibility of achieving high-resolution separations of medium polarity compounds using nonpolar carbon dioxide as the mobile phase in SFC and the successful coupling of SFC to MS to obtain mass chromatograms and reliable chemical ionization mass spectra. High resolution separations of the polycyclic aromatic hydrocarbon fractions of marine diesel fuel samples were combined with isobutane chemical ionization MS. Analysis of the more polar components will require a more polar supercritical fluid mobile phase.

INTRODUCTION

Recently, the interest and use of supercritical fluid phenomena in analytical methods have increased. A number of potentially important techniques have emerged which include capillary-column supercritical fluid chromatography (SFC)¹⁻⁵ capillary-column supercritical fluid chromatography-mass spectrometry (SFC-MS)^{6,7}, direct fluid injection-mass spectrometry (DFI-MS)^{8,9} and direct supercritical fluid extraction-mass spectrometry (SFE-MS)^{10,11}. While these techniques are in a relatively early stage of development, they have already shown considerable potential for providing important contributions to the characterization of complex mixtures.

The potential advantages of SFC accrue from the nature of the supercritical fluid. The compressibility of supercritical fluids is large above the critical temperature and small changes in pressure result in large changes in the density of the fluid¹². The

density of a supercritical fluid is typically 10^2 to 10^3 times greater than that of the gas¹². Consequently, molecular interactions increase due to shorter intermolecular distances. This imparts solubilizing characteristics similar to liquids, but with significantly lower viscosities and higher diffusion coefficients¹². The lower viscosities and higher diffusion coefficients result in the potential for significantly enhanced chromatographic efficiency per unit time relative to liquid chromatography. Since the density of supercritical fluids is several hundred times greater than that of a gas, the potential for separation of higher-molecular-weight compounds relative to gas chromatography (GC) is possible. In addition, the mild thermal conditions (determined by the choice of SFC mobile phase) allow the application to thermally labile compounds. Furthermore, accurate control of the solvating power of the mobile phase is possible since it is dependent on pressure. Thus, in capillary SFC where the pressure drop across the column length is minimal, pressure (or density) programming can be used in an analogous manner to temperature programming in GC and gradient elution in liquid chromatography. Current capillary-column technology utilizing 50- μm I.D. columns coated with non-extractable stationary phases offers high chromatographic efficiency (> 3000 effective plates per meter) which allows high-resolution separations comparable to capillary GC. The use of capillary columns also simplifies interfacing SFC to MS since the total column effluent can be injected directly into the mass spectrometer. The advantages of SFC-MS compared to high-performance liquid chromatography (HPLC)-MS have been described previously^{6,7,13,14}.

This paper describes the successful application of SFC and SFC-MS to the analysis of selected marine diesel fuel (MDF) samples. High-resolution separations of the polycyclic aromatic hydrocarbon fractions of two diesel fuels were achieved by SFC. SFC-MS was also used to obtain mass selective detection and acquire high quality chemical ionization (CI) mass spectra. The application of non-polar supercritical carbon dioxide restricted the present work to characterization of the less polar and moderately polar fractions. Although these analyses could have been accomplished by GC and GC-MS, this work illustrates the potential of these new techniques and the impetus for extension to more polar fluid systems which have already been demonstrated to be compatible with the mass spectrometer interface⁹.

EXPERIMENTAL

Samples and sample preparation

Two MDF samples provided by the U.S. Naval Research Laboratory were used for these studies. They consisted of a relatively unstable, sediment-forming fuel (81-6), and a typical stable fuel (81-5). They were stored in glass bottles at *ca.* 4°C after receipt until used.

The polycyclic aromatic hydrocarbon fractions were obtained using alumina adsorption chromatography¹⁵. Briefly, approximately 0.2 g of fuel was adsorbed onto 3 g of neutral alumina and packed on top of a column already containing 6 g of the same alumina. After elution with 20 ml of hexane to remove the aliphatic and monocyclic aromatic components, the polycyclic aromatic hydrocarbons were eluted with 50 ml of benzene. A detailed description of these materials and the fractionation procedure has been given elsewhere¹⁶.

Supercritical fluid chromatography

The instrumentation used for SFC is similar to that previously described^{3,7}. The SFC apparatus utilized a modified Varian 8500 syringe pump to generate high pressure and pulse-free mobile phase supplies and a modified Hewlett-Packard 5700 gas chromatograph oven to provide constant temperature conditions. Pump control and pressure ramping conditions were controlled with a microcomputer to generate linear density gradients as a function of pressure. A more detailed discussion of density control as a function of pressure at various temperatures is described elsewhere¹⁷. For supercritical carbon dioxide which was used as the mobile phase in this study, density ramp profiles ranging from reduced densities of 1.01 to *ca.* 1.6 were used which corresponded to pressures ranging from approximately 73 to 200 atm. at the operating temperature of 60°C (a reduced temperature of 1.10). Sample introduction was accomplished using a Valco C14W HPLC injection valve equipped with a 0.1- μ l rotor. The injection valve was mounted exterior of the oven and the chromatographic column connected through a "splitter", described previously¹⁸. The restriction on the split vent was adjusted to allow approximately a 1:20 flow into the chromatographic column. Chromatographic columns consisted of 15–20 m \times 50 μ m I.D. fused-silica capillary tubing coated with approximately 0.25- μ m film-thickness of a 50% phenyl polymethylphenylsiloxane phase which had been stabilized and rendered non-extractable by extensive crosslinking¹⁹. Flame ionization detection (FID) was accomplished with a standard Hewlett-Packard 5711 flame ionization detector. To obtain maximum sensitivity, the hydrogen/air ratio was optimized and the detector operated in the most sensitive range. Prior to detection the supercritical fluid was decompressed and the mobile phase linear velocity controlled to approximately 1.5 cm/sec by connecting the terminal end of the chromatographic column to a short length (*ca.* 25 mm) of 5- μ m I.D. fused-silica restrictor column. The detector body was heated to 350°C. Since FID was used, it was necessary to remove any trace hydrocarbon impurities and purify the carbon dioxide mobile phase to prevent serious baseline drift during pressure ramping conditions. This was done by distilling liquid carbon dioxide into the pump while passing it through activated charcoal and alumina adsorbents.

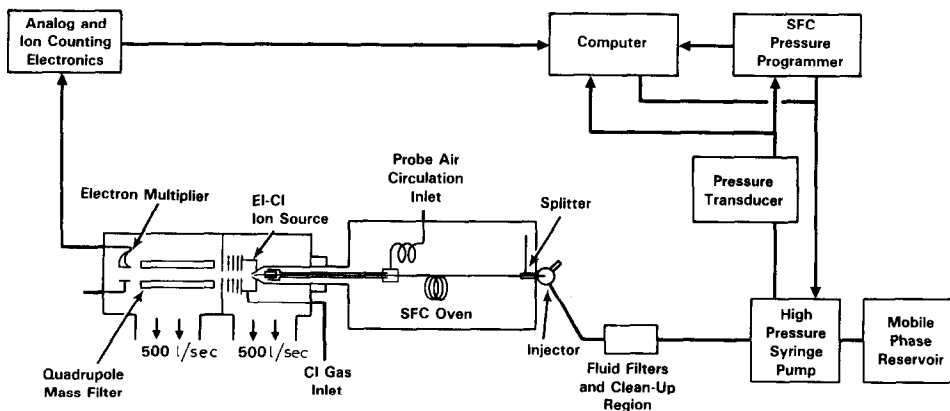


Fig. 1. Schematic diagram of the SFC-MS instrumentation.

Supercritical fluid chromatography-mass spectrometry

The instrumentation used for SFC-MS has been described in detail elsewhere^{6,7,9,14}. A schematic diagram of this instrumentation is shown in Fig. 1. Supercritical carbon dioxide was used as the supercritical mobile phase and isobutane for the CI reagent gas. The chromatographic portion of the system was similar to that described above for SFC. The chromatographic column was extended through an air heated probe which was used for insertion into the mass spectrometer¹⁴. Careful temperature regulation of the probe was achieved by forcing oven-heated air along the probe length. The column extended to within a few cm of the probe tip where a short length (10–25 mm) of 5- μ m I.D. fused-silica tubing was connected to function as a depressurization zone and form the interface between supercritical and CI vacuum conditions. The linear velocity of the supercritical mobile phase was also regulated in this manner to between 1 and 2 cm/sec. Typical CI mass spectrometer operating conditions were utilized (*e.g. ca.* 0.8 torr ion-source pressure). For these separations the mass spectrometer was scanned over the range of 120 to 300 a.m.u. at 2.75 sec per scan.

RESULTS AND DISCUSSION

Supercritical fluid chromatography

Presently, carbon dioxide is the most convenient fluid for capillary SFC. This results from its low critical temperature ($T_c = 31^\circ\text{C}$) and its chemical inertness to the chromatographic system, the stationary phase, and sample solutes. It is also compatible with FID. Supercritical carbon dioxide has sufficient solvent strength to elute moderately polar compounds of somewhat lower volatility than is possible with GC. However, for non-polar compounds this range is extended and significantly higher-molecular-weight components can be successfully eluted.

Chromatograms of the slightly polar polycyclic aromatic hydrocarbon fractions obtained from the alumina separation of MDF 81-5 and 81-6 are compared in Fig. 2. These high-resolution separations are comparable to those achievable using high-resolution capillary gas chromatography with only little increase in analysis time. FID provided excellent sensitivity and a near universal response. A highly cross-linked 50% phenyl polymethylphenylsiloxane stationary phase was used which provided the necessary stability to withstand the solvating influence of the supercritical fluid. A 60°C operating temperature provided a more convenient density-pressure relationship and allowed more precise control of the mobile phase solvating power than lower temperatures. Dual ramp, linear density programs were utilized for these separations. The samples were injected at a density of 0.17 g/ml (*ca.* 73 atm) which was held constant for 20 min while the solvent peak eluted. The density was then increased at 0.003 g/ml per min for 30 min to a density of 0.26 g/ml and then at 0.007 g/ml per min for an additional 40 min to a final density of approximately 0.72 g/ml. This dual ramp density profile provided near optimum elution conditions to achieve good separation over the entire range of sample components.

The chromatographic profiles of the sample components in these two fuels were almost identical with only minor differences of composition observable. The significant chemical differences between the stable and unstable fuels are most likely in the more polar components rather than the polycyclic aromatic hydrocarbon com-

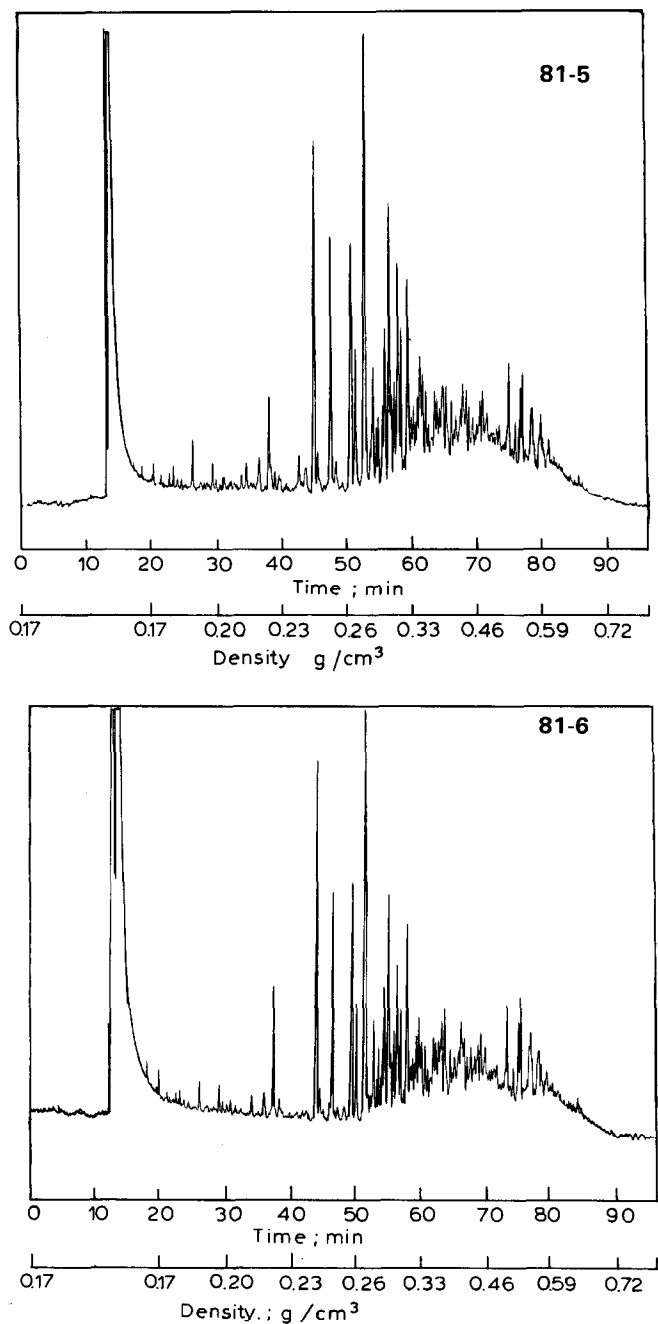


Fig. 2. Capillary supercritical fluid chromatograms of the polycyclic aromatic hydrocarbon fractions of MDF 81-5 and MDF 81-6 samples. See text for chromatographic conditions.

ponents. The initial application of direct DFI-MS with highly polar fluids for characterization of these materials is described elsewhere²⁰,

Supercritical fluid chromatography-mass spectrometry

SFC-MS was also used to analyze selected fuel samples. The total-ion chromatogram obtained from the SFC-MS analysis of the polycyclic aromatic hydrocarbon fraction of the 81-6 fuel is shown in Fig. 3. This separation was obtained using essentially the same chromatographic conditions as was used for the separation shown in Fig. 2 except a linear pressure ramp was utilized instead of a linear density ramp. Although, the chromatographic resolution in this separation was lower (due to increasing pressure instead of increasing density), the overall quality of the separation was comparable to that achieved using FID. In general, the isobutane chemical ionization conditions formed predominately $[M + 1]^+$ ions with smaller amounts of $[M + 43]^+$ ions. The solvent peak is small since the molecular ion for carbon dioxide was not in the mass range scanned (however, trace impurities in the carbon dioxide were detected) and also since carbon dioxide has a lower proton affinity than iso-

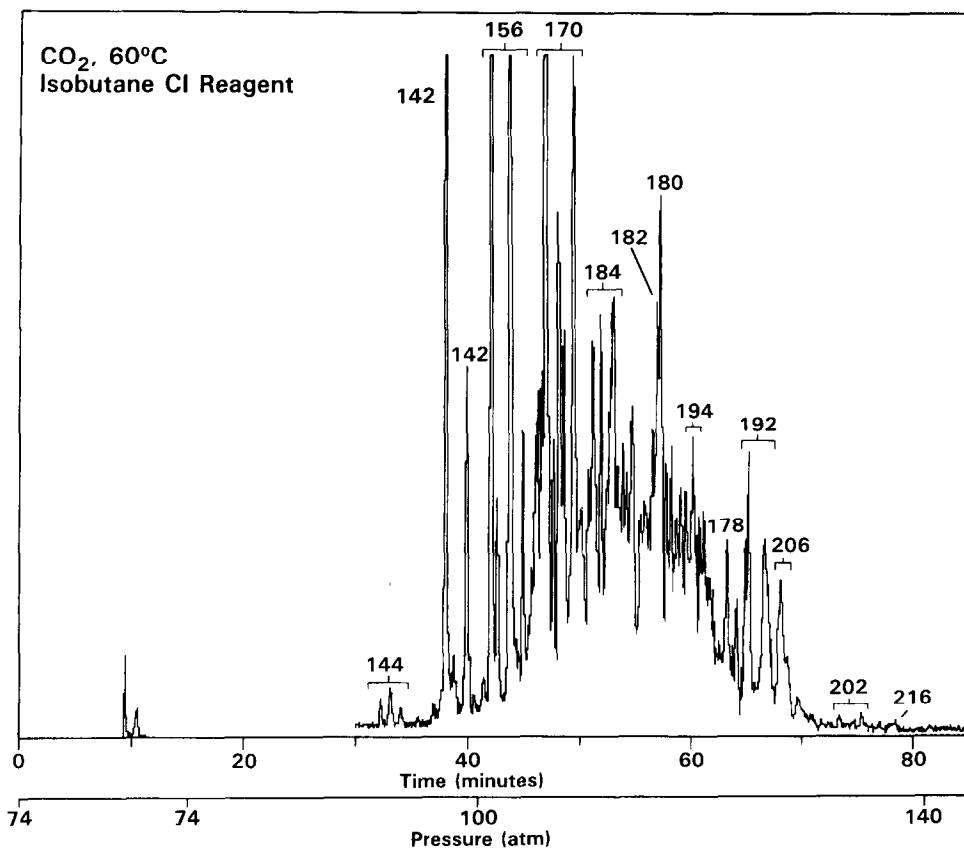


Fig. 3. Total-ion chromatogram obtained from the capillary SFC-MS analysis of the polycyclic aromatic hydrocarbon fraction of MDF 81-6. Peak labels refer to the actual molecular weight of the compounds. See text for experimental conditions.

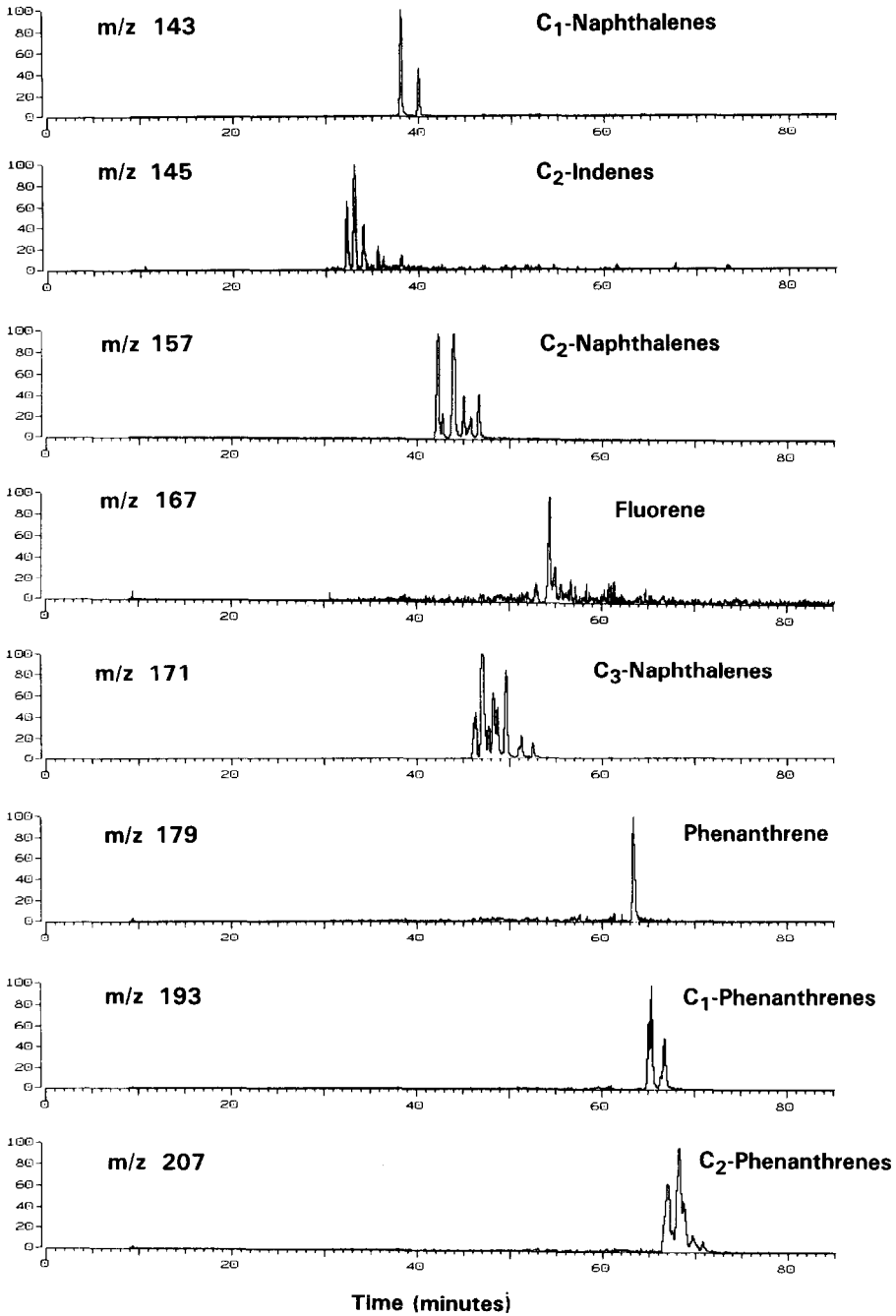


Fig. 4. Typical single-ion chromatograms for selected masses for the SFC-MS analysis described in Fig. 3.

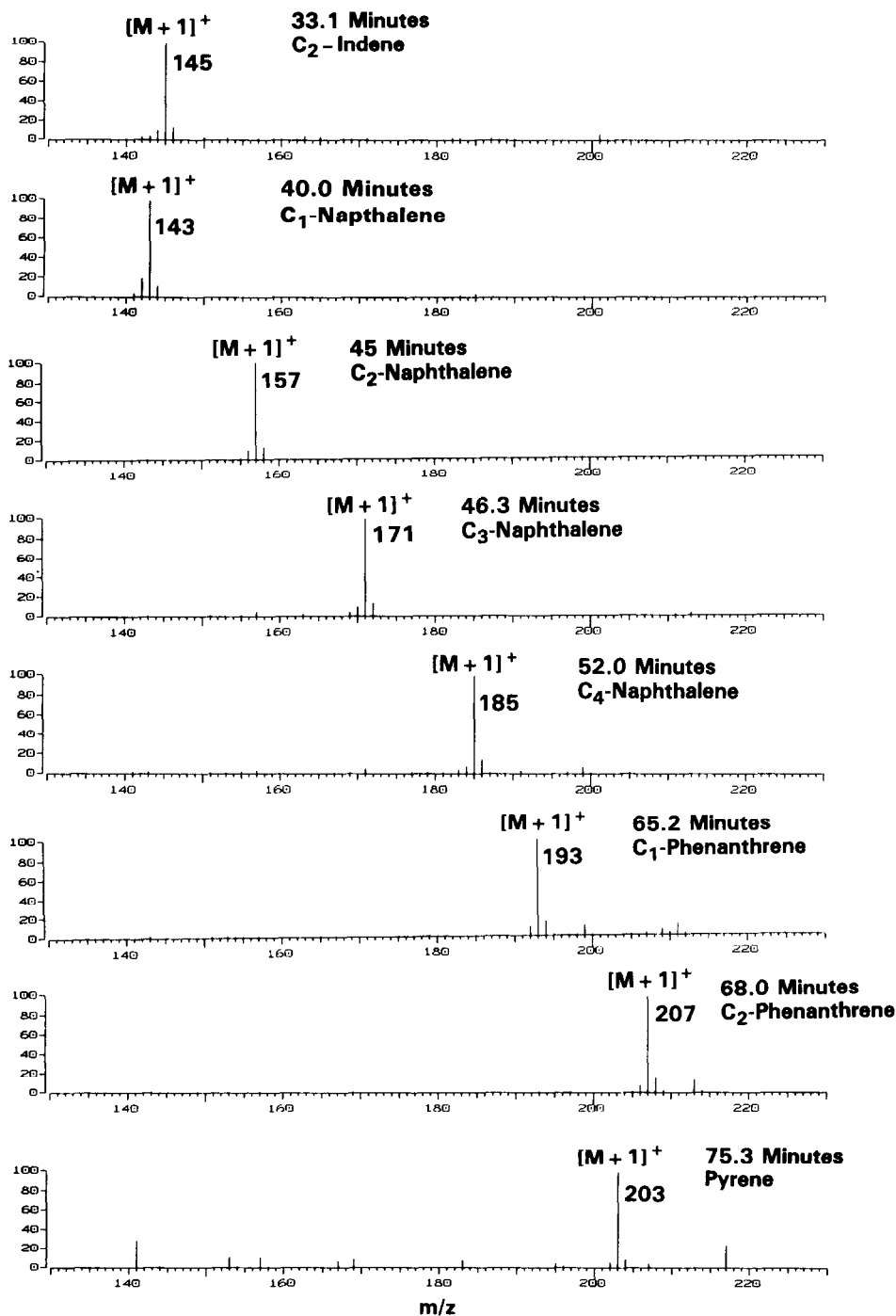


Fig. 5. Typical isobutane CI mass spectra obtained for selected peaks from the SFC-MS analysis described in Fig. 3.

butane. (The chromatographic baseline is absent before and after the solvent peak because signal data were only stored while sample components were being eluted.)

Typical single-ion chromatograms obtained from this analysis are shown in Fig. 4. Since the protonated molecular ions, or $[M + 1]^+$ ions, are at odd m/z values, the molecular weights of the components are even. Tentative identifications based on molecular weight and chromatographic retention time for these components are also included on each single-ion chromatogram. Similar, but lower intensity, profiles (not shown) were obtained for m/z 149, m/z 155, m/z 159, m/z 163, m/z 169, m/z 177, m/z 181, m/z 183, m/z 185, m/z 191, m/z 195, m/z 197, m/z 199, m/z 203, m/z 209, m/z 211, m/z 213, m/z 217 and m/z 219. Some typical chemical ionization spectra obtained at selected times in the SFC-MS analysis are shown in Fig. 5. The mass spectra show dominant $[M + 1]^+$ signals, suggesting that good CI conditions were achieved and that reliable mass spectra were obtained. These spectra are useful for assigning molecular weights to the unknown components and, when used in conjunction with chromatographic retention times, serve as a basis for actual component identifications. The material in this fraction consists essentially of two and three ring neutral polycyclic aromatic hydrocarbons and numerous isomers of their alkylated homologs. Various alkylated isomers of monocyclic aromatic compounds are also present (e.g. substituted benzenes and tetralins). Exact identifications of the many isomers present would require retention data obtained from chromatographing individual standards for each component.

The present work demonstrates the potential of capillary SFC-MS for analysis of complex fuel mixtures. Both high-resolution separations and high-quality CI mass spectra were obtained. The extension of these techniques to more polar fluid systems should allow characterization of the more interesting polar fuel components.

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