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Technical Progress Report for the period
October 1, 1985 - September 30, 1986

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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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DEVELOPMENT AND EVALUATION OF SUPERCRITICAL FLUID CHROMATOGRAPHY/MASS SPECTROMETRY FOR POLAR AND HIGH-MOLECULAR-WEIGHT COAL COMPONENTS

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October 1, 1985 - September 30, 1986

E. K. Chess
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Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

This program, Development and Evaluation of Supercritical Fluid Chromatography/Mass Spectrometry for Polar and High-Molecular-Weight Coal Components, is funded through DOE Office of Fossil Energy, Advanced Research and Technology Development Branch, Morgantown Energy Technology Center. It is aimed at the development of new analytical technologies for the characterization of previously intractable complex mixtures. The specific goals of this program are twofold: 1) to develop and evaluate a combined high-resolution, capillary column, supercritical fluid chromatograph/high-performance mass spectrometer (SFC/MS) that is capable of analyzing high-molecular-weight materials, such as polar and heavy-end components found in coal conversion processes; and 2) to use this system to develop and evaluate analytical technology applicable to coal process development technology. Polar fluid systems most appropriate for polar and heavy-end materials will also be developed and evaluated. This program is expected to provide a greatly improved characterization of complex high-molecular-weight and polar materials, and to determine the feasibility of using SFC/MS methods for on-line characterization of coal conversion processes. The effort includes evaluation of quantitative instrumental approaches, of various ionization modes, and of tandem mass spectrometric techniques for analyzing individual components in complex mixtures. The effort will define the range of applicability and utility of high-performance SFC/MS methods.

During FY 1986, technical progress toward the programmatic goals of developing and evaluating SFC/MS for the analysis of higher-molecular-weight compounds was made in the following areas:

- Studies have been conducted to characterize the requirements for and to facilitate the transfer of thermal energy to the capillary flow restrictor region. Such studies have resulted in a new interface probe design.
- The redesigned interface probe was constructed and tested. The new design was shown to allow better transport of higher molecular weight, less volatile compounds than the previous design, decreasing

the mass discrimination occurring at the supercritical fluid chromatograph mass spectrometer interface region.

- Methods allowing the mass calibration of the magnetic sector mass spectrometer to 1400 daltons have been developed.
- A digital syringe pump controller, interfaced to an Apple IIe computer has been substituted for the previous analog pump control unit, allowing much finer and more reproducible control of the pressure (density) of the supercritical fluid mobile phase.
- Relative nonpolar supercritical fluid mobile phases have been modified by the addition of small amounts of polar fluids to create fluids with higher solvating powers than, but with similar operating parameter to, the non-modified fluids. Results from characterization experiments indicate an in-depth knowledge of the modified fluid behavior is required for successful utilization of these modified fluids.
- Polar-modified fluids have been used with the magnetic sector mass spectrometer in experiments using three types of supercritical fluid introduction to the mass spectrometer: direct fluid injection, supercritical fluid chromatography, and supercritical fluid extraction with high mass resolution.
- Capillary columns were exposed to various polar-modified mobile phases and evaluated for stability. The test results indicated that our present methods for preparing columns are sufficient, for many of the stationary phase and supercritical fluid combinations tested, to create columns that can be successfully used with supercritical fluid chromatography.

CONTENTS

FIGURES

TABLES

LIST OF ABBREVIATIONS

^{252}Cf-PDMS	^{252}Cf-plasma desorption mass spectrometry
AMW	average molecular weight
CI	chemical ionization
DAS	diacetoxyscrirpenol (or trichothecene mycotoxin)
DCI	desorption chemical ionization
DFI	direct fluid injection
DFI/MS	direct fluid injection/mass spectrometry
DOE	Department of Energy
EI	electron impact ionization
FAB	fast atom bombardment
FD	field desorption
FID	flame ionization detector
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
ID	inside diameter
LD	laser desorption
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MW	molecular weight
PAH	polynuclear aromatic hydrocarbon
PEG	polyethylene glycol
RHT	restrictor heater temperature
SFC	supercritical fluid chromatography
SFC/MS	supercritical fluid chromatography/mass spectrometry
SFE	supercritical fluid extraction
SIMS	secondary ion mass spectrometry
SS	stainless steel
ZDV	zero dead volume (seal)

INTRODUCTION AND PROGRAM GOALS

This program, funded through DOE Morgantown Energy Technology Center, is aimed at the development of new analytical technologies for the characterization of previously intractable complex mixtures. The specific goals of this program are twofold: 1) to develop and evaluate a combined high-resolution, capillary column, supercritical fluid chromatograph/high-performance mass spectrometer (SFC/MS) that is capable of analyzing high-molecular-weight materials, such as polar and heavy-end components found in coal conversion processes; and 2) to use this system to develop and evaluate analytical technology applicable to coal process development technology. Polar fluid systems most appropriate for polar and heavy-end materials will also be developed and evaluated. This program is expected to provide a greatly improved characterization of complex high-molecular-weight and polar materials, and to determine the feasibility of using SFC/MS methods for on-line characterization of coal conversion processes. The effort includes evaluation of quantitative instrumental approaches, of various ionization modes, and of MS/MS techniques for analyzing individual components in complex mixtures. The effort will define the range of applicability and utility of high-performance SFC/MS methods.

BACKGROUND

A supercritical fluid is a substance at a temperature above its critical temperature, where a distinct liquid phase cannot exist. At high pressures above the critical temperature, the resulting fluid or "dense gas" will attain densities approaching that of a liquid, with increased intermolecular interactions, and will begin to assume some of the properties of a liquid. By increasing the pressure of a supercritical fluid, its properties may be varied continuously from those of a gas to those of a dense fluid with the solvating power of a liquid. The combination of gaseous and liquid properties can be used to advantage with supercritical fluids as mobile phases in chromatography and as a transport medium for sample introduction in MS. Supercritical fluids have also shown a potential for important advances in separating and fractionating nonvolatile or thermally labile compounds. The potential for improved chromatographic methods has been recognized for two decades. With the development of capillary columns suited for SFC, this potential has finally begun to be realized.

Supercritical fluid chromatography can separate nonvolatile and thermally labile compounds that are impossible to separate by gas chromatography (GC). The introduction of nonvolatile or thermally labile compounds for mass spectrometric analysis is an important area of research in MS. Current methods for introducing and analyzing such compounds include field desorption (FD), desorption chemical ionization (DCI), laser desorption (LD), and a suite of particle bombardment techniques, such as secondary ion mass spectrometry (SIMS), fast atom bombardment (FAB), and ^{252}Cf-plasma desorption mass spectrometry (^{252}Cf-PDMS). However, these methods are subject to difficulties, including matrix effects, complex mass spectra, responses that vary greatly with compound polarity, difficult quantitation, spectra that are difficult to predict and interpret, and sensitivity to the nature of the substrate support surfaces. The development of the direct fluid injection (DFI) interface at Pacific Northwest Laboratory has resulted in establishing methods for the direct characterization of supercritical fluids, as well as demonstrating the feasibility of the combined capillary column SFC/MS (Smith et al. 1982; Smith, Fjeldsted, and Lee 1982; Smith and Udseth 1983a,b,c; Smith, Wright, and Udseth 1983; Smith, Wright and Udseth 1984). This approach allows relatively high molecular weight compounds to be efficiently separated and analyzed, with detection limits generally in the picogram range (Smith and Udseth 1983a). Our work has shown that excellent "soft" chemical ionization (CI) spectra, amenable to quantitation, can be obtained for any compound soluble in a supercritical fluid.

When this program was initiated, capillary SFC development work had been limited to the analysis of relatively low molecular weight and less polar components. These SFC systems were compatible with the limitations of low-resolution quadrupole mass spectrometers of limited mass range used as detectors. However, modern coal conversion processes have analytical chemistry needs that include the analysis of high-molecular-weight and/or polar organic compounds found in extremely complex mixtures. Analytical techniques that are capable of such analyses and that are also compatible with on-line process monitoring are highly desirable. Current synfuels process monitoring techniques provide information about reaction conditions and bulk characteristics of the process materials, such as temperature, pressure, reactant gas (hydrogen) metering, and mass balance. Such information gives the process engineer some insight as to how the process is operating in general, but does not provide the detailed chemical information about the process materials that is ultimately required in order to determine the success of the process or improvement strategies. On-line process monitoring by GC is used by the chemical industry, and recently in coal liquefaction processes, for the analysis of gases and relatively volatile chemical components of feed and product lines in production processes that require careful process control. However, the heavy-molecular-weight, relatively nonvolatile components are not monitored in detail in industrial processes due to the lack of appropriate instrumentation. Similar problems apply to any process in which high molecular weight mixtures may be present. A goal of this program is the development and evaluation of new methods, based upon approaches using supercritical polar fluid systems and high-performance SFC/MS, for characterizing complex mixtures that contain components not amenable to analysis by conventional approaches (e.g., GC/MS).

PROGRAM DESCRIPTION

The program can be conceived as having three distinct sub-phases of instrument development, a phase of development and evaluation of capillary column technology, and a phase of development and critical assessment of analytical potential. The three instrument development sub-phases are defined here and described in the following paragraphs: 1) design and fabrication of the supercritical fluid chromatograph, SFC/MS interface, and MS ion source, and any modifications of the mass spectrometer to allow compatibility; 2) performance evaluation of the instrumentation using supercritical fluids and test compounds of varying polarity; and 3) use of the instrumentation to develop analytical methodologies for the characterization of previously intractable components of complex mixtures, with an initial emphasis on the analysis of coal conversion materials.

The instrument design and fabrication sub-phase incorporated information gained from the successful interfacing of supercritical fluid chromatographs to quadrupole mass spectrometers into the design of a chromatograph and interface suited to the additional demands imposed by a magnetic sector mass spectrometer. The magnetic sector, high resolution mass spectrometer was chosen as the detector because of its extended mass range (up to 7000 amu), high resolution capability, sensitivity for higher masses, and potential for characterization of individual components in complex mixtures by tandem mass spectrometry (MS/MS) techniques.

The instrument evaluation sub-phase was to commence during the design and fabrication phase, and results from the evaluation were to be used to further modify the instrumentation in order to improve its performance. The instrumentation evaluation was to begin with the analysis of relatively nonpolar compounds, such as alkanes and polynuclear aromatic hydrocarbons, using nonpolar supercritical fluids, such as pentane and carbon dioxide. The evaluation would then proceed to the analysis of relatively polar components of higher molecular weight using more polar fluids, such as methanol and ammonia. During this phase of the project, the instrumentation would also be used to aid in the development of capillary column technology aimed at producing stationary phases and bonded-phase columns suitable for use with polar fluids. This column technology development and evaluation phase will continue for the life of the project, beyond the instrument evaluation phases.

After the instrumentation has been sufficiently developed, the analysis of higher molecular weight and polar materials from a variety of sources will commence. The sample sources will include, but not be limited to, heavy end and refractory materials from coal conversion processes that have proved intractable by conventional analyses. Where possible, the results will be compared with those from other forms of analyses to determine the extent of the anticipated enhanced level of characterization. Other materials to be examined will include those of special interest to other DOE programs. This sub-phase will include the development of analytical methodologies for the characterization of a wide variety of materials, and will define the role and limitations of the SFC/MS technologies. This information will be used to critically assess the role that SFC/MS and related technologies might have in on-line process monitoring, and aid in the design of such monitoring systems.

TECHNICAL PROGRESS

The technical progress of the second full year (months 19 through 31) of this program, from the end of FY 1985 to the end of FY 1986, will be reviewed in this fourth-quarter Technical Progress Report for FY 1986. The progress achieved will be discussed in general topic areas, as was the format for the Technical Progress Report for FY 1985, not as specific program tasks, as has been the format in previous Technical Progress Reports. The first topics discussed cover aspects of improving the performance of the instrumentation, such as optimizing the the capillary flow restrictor performance, improving the design and function of the supercritical fluid chromatograph-mass spectrometer interface region, developing methods for mass calibration, and improving the solvent delivery system. A discussion of the use of polar-modified mobile phases in capillary supercritical fluid chromatography follows. This discussion leads into the final topics detailing the progress made toward the the use of polar supercritical fluids with the magnetic sector mass spectrometer and the development of the technology required to create and evaluate capillary chromatographic columns suitable for use with polar mobile phases.

RESTRICTOR PARAMETER OPTIMIZATION

Methods have been described in previous reports for reproducibly fabricating a tapered fused silica restrictor to serve as a decompression zone for fluid expansion into the mass spectrometer ion source and to control linear velocity of the supercritical mobile phase. It has been established that tapered restrictors facilitate transfer of analyte molecules to the gas phase by minimizing the rate of density change (and change in solvent strength) along the length of the restrictor and by improving heat transfer to the fluid through the thinner capillary walls (Chess and Smith 1986). Silica is a good thermal insulator and, because in most cases cooling occurs during the fluid expansion, heat input is generally necessary to prevent precipitation of the analytes.

Studies have been conducted to optimize and facilitate heat transfer to the restrictor region to compensate for the cooling effects during expansion.

These studies have centered around preheating the fluid in a short length of uncoated (but deactivated) fused silica tubing that is connected between the analytical column and the restrictor. Heating has generally been accomplished by placing the fused silica in a tight-fitting stainless steel (SS) capillary tube and passing a current through the stainless steel. At lower detector temperatures and with higher molecular weight analytes, heating of the mobile phase to temperatures greater than the chromatographic operating temperature would improve analyte transmission through the restrictor. This process appears to be a viable method for supplementing the heat transfer to the restrictor. Other studies using metal coatings on the fused silica restrictors have not yet provided any definitive conclusions.

The effect of restrictor heater temperature on the detection of a butadiene polymer separation is shown in Figure 1. At the higher restrictor heater (detector) temperature, a significantly larger range of polymer oligomers was successfully detected. The separations were accomplished on a 5 m x 50 μm column coated with SE-54 stationary phase and a carbon dioxide mobile phase at 100°C. The fluid pressure was programmed from 72 to 360 bar at approximately 5.5 bar/min. Flame ionization detection (FID) was utilized. In general, analyte transfer to the gas phase from a supercritical fluid expansion is aided by increased temperature when the compounds exhibit increased volatility with temperature. For truly nonvolatile compounds, increased temperatures may lead to poorer detectability. This is illustrated by the results of experiments in which different restrictor temperatures were utilized during the separation of a nonvolatile polymer, polycarbosilane (see Figure 2). Although good detectability was never achieved, the trend is clear that, at higher restrictor temperatures, poorer detectability occurred as evidenced by increased clustering and "spiking," and finally by the complete loss of signal as the analyte precipitated. Excessive loss of analyte can also lead to restrictor plugging. These results indicate that various approaches are needed to optimize the restrictor and the interface operating conditions, both of which are dependent on the chemical characteristics of the analyte.

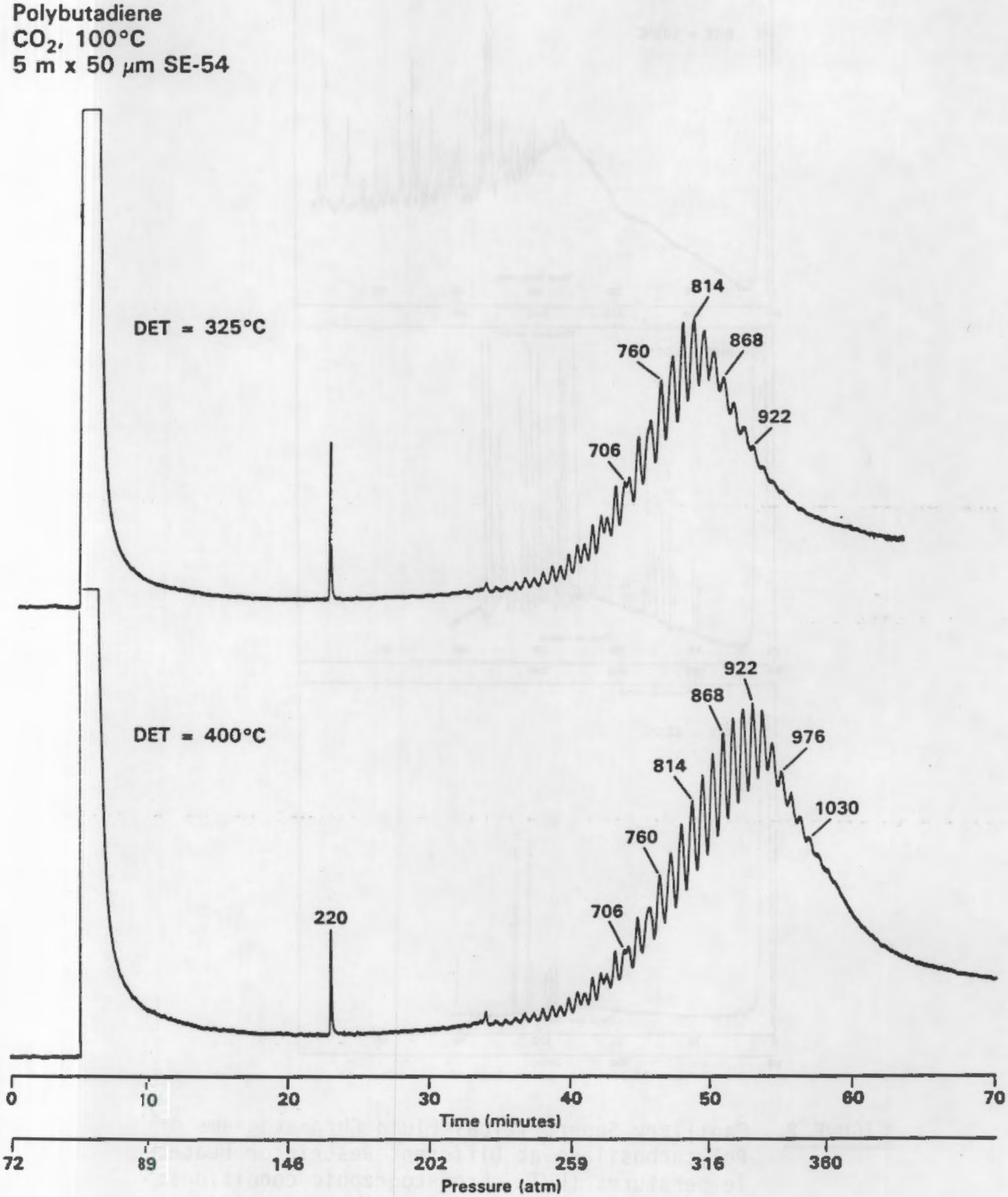

FIGURE 1. Capillary Supercritical Fluid Chromatograms of Polybutadiene Using Different Restrictor Temperatures (see text for chromatographic conditions)

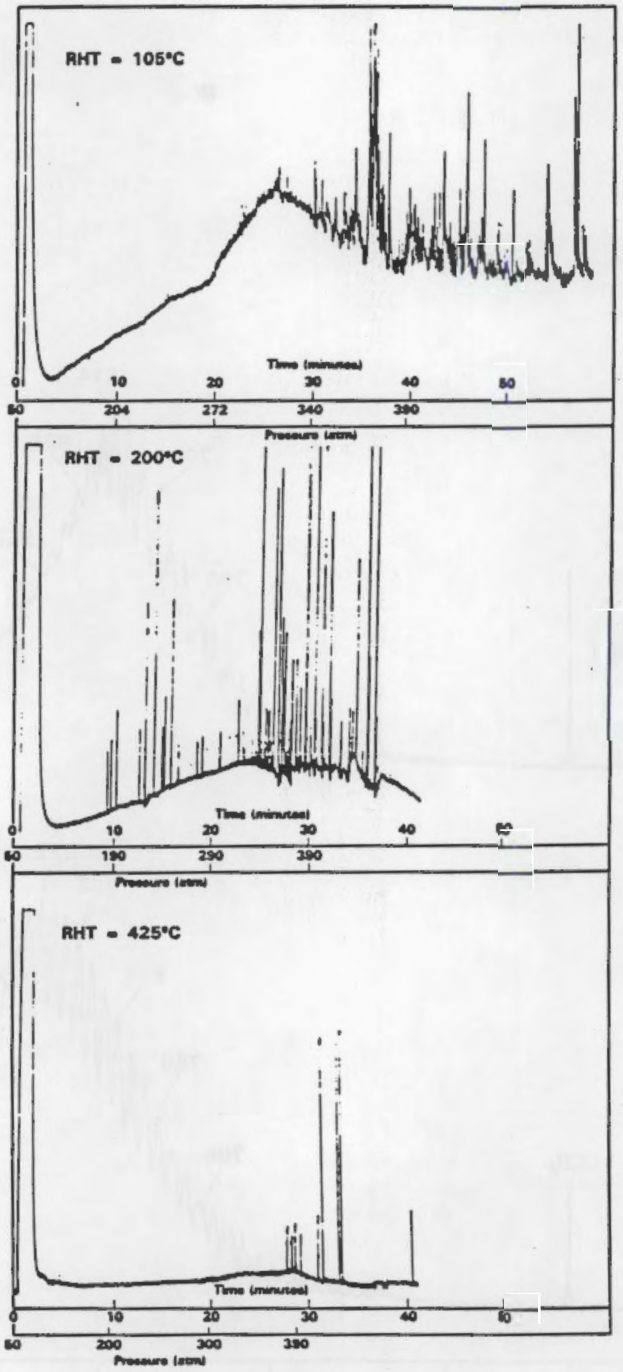

FIGURE 2. Capillary Supercritical Fluid Chromatograms of Polycarbosilane at Different Restrictor Heater Temperatures (RHT, chromatographic conditions: 5m x 50-μm-ID SE-54 column, carbon dioxide mobile phase at 150°C)

DEVELOPMENT OF AN IMPROVED SFC/MS INTERFACE

A major effort of the research in this program has been directed toward investigating the nature and causes for the experimentally observed discrimination against the transport of higher-molecular-weight (molecular weights in excess of 300 daltons) polynuclear aromatic hydrocarbons (PAH) through the supercritical fluid flow restrictor and into the ion source of the mass spectrometer. Mixtures of PAH containing compounds as high in molecular weight (MW) as coronene (MW 300), decacyclene (MW 450), and rubrene (MW 532) have been chromatographed successfully in our laboratory using supercritical pentane and detected on-column (with fluorescence detection) just prior to exiting the chromatographic column through the flow restrictor. These results indicated that the high-molecular-weight material was being transported to the end of the column, but was probably not passing through the flow restrictor. SFC experiments with a flame ionization detector (FID) showed that the restrictor discrimination against higher-molecular-weight materials decreased as the temperature of the FID was increased. Results from experiments conducted with quadrupole SFC/MS instruments indicated that the mass discrimination problem could be diminished if the flow restrictor was in intimate contact with the flow restrictor heater. Modifications were made to the flow restrictor heater and to the interface probe tip with the aim of improving the heat transport to the fused silica flow restrictor. However, these modifications resulted in a loss of the electrical isolation required between the interface probe shaft and the ion source. Therefore, a new interface probe was designed that 1) incorporated a 0.015-in.-ID SS capillary tube as the flow restrictor heater; 2) allowed the temperature of the heater to be measured by a thermocouple mounted at the hottest spot; and 3) better electrically isolated the probe tip, which is held at the ion source accelerating potential, from the electrically grounded interface probe shaft.

A schematic diagram of this new interface probe is shown in Figure 3. The SS probe tip houses the SS capillary flow restrictor heater (which is silver-soldered into the probe tip) and serves as one electrical contact point for the heater. The second electrical connection to the restrictor heater is made approximately 1.5 cm from the silver-soldered joint, making the heated portion

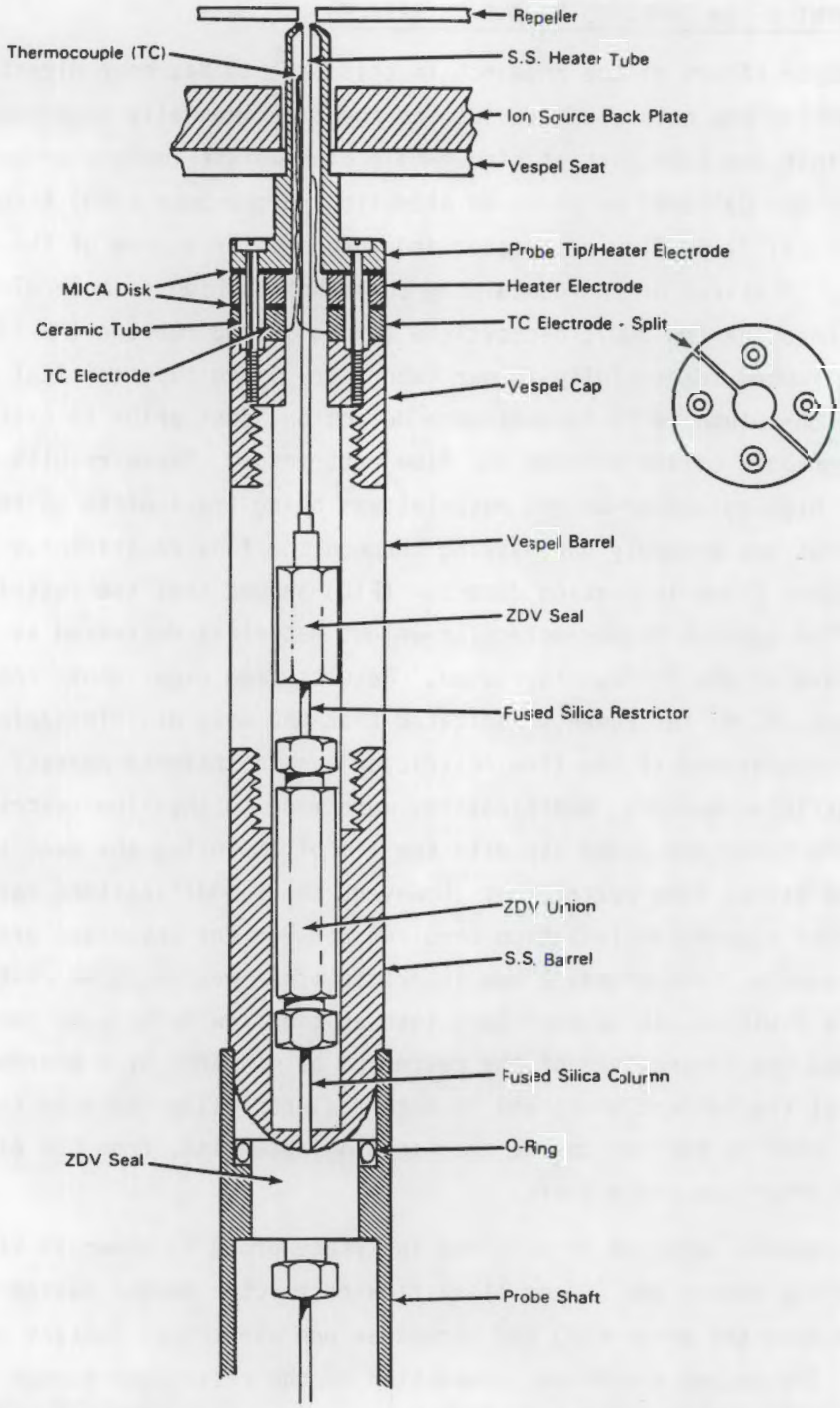

FIGURE 3. Schematic Diagram of the Redesigned SFC/MS Interface Probe

approximately 1.5 cm in length. A chromel/alumel thermocouple is silver-soldered to the SS capillary tube at the midpoint of the heater region. The heater lead wire is connected to the heater electrode ring, which is electrically isolated from the probe tip by a thin sheet of mica. The two thermocouple leads are connected to the split thermocouple electrode ring, which is electrically isolated from the heater electrode by a mica disk. The probe tip/electrode assembly is held together by four screws that are sheathed by ceramic tubes and screwed into a Vespel® (DuPont) end cap. The electrical connections to the electrodes are made by copper spring contact points mounted on the ion source support structure (not shown) when the interface probe is inserted into the vacuum system and mated against the ion source.

The SS capillary tube extends through the end cap and is silver-soldered into the nut of a zero-dead-volume (ZDV) seal, which is used to make a gas-tight seal between the interior of the interface probe and the ion source volume. This ZDV seal is held at ion source accelerating potential, and is housed by the Vespel® barrel in order to electrically isolate it from the SS barrel and the ZDV union. The ZDV union is used to couple the capillary flow restrictor to the SFC column. The column enters the interface region from the interior of the probe shaft. The vacuum seal between the probe shaft interior and the interface region interior is made with an O-ring around the SS barrel and a ZDV seal around the capillary column. The interior of the interface region is open to the vacuum of the ion source housing, which provides additional electrical isolation between the high accelerating potential and the electrically grounded probe shaft.

The copper spring contact points are mounted on the ion source support such that they are electrically isolated from the support by ceramic insulators. Ceramic-insulated copper wires connect the spring contacts to the electrical feedthroughs on the ion source back flange. The ion source was modified in order to accommodate the new interface probe by 1) replacing the repeller/heater assembly with a repeller plate containing only a small hole in place of the heater, 2) enlarging the hole in the ion source back plate to allow the larger diameter probe tip to be inserted into the ion source volume, and 3) replacing the ceramic adapter block with a thin Vespel® plate. When the newly designed interface probe is mated with the modified ion source, the tip of the interface probe, containing the flow restrictor heater and thermocouple, is located immediately behind the repeller plate, and the hole in the probe tip is aligned with the hole in the repeller plate.

Initial testing of the new interface was performed using isopentane as the supercritical fluid, at 220°C and 30 to 70 atm pressure. It was determined that small leaks in the ZDV fittings led to electrical breakdown at accelerating (ion source) voltages higher than 1000 V, which provided a sensitive means of assessing the "leak-tightness" of the plumbing in the new probe tip assembly. When all seals are functioning properly, the electrical breakdown from the ion source to the supercritical fluid chromatograph is now only a problem when operating the ion source at accelerating potentials greater than 6000 V, which is a marked improvement over the previous probe design, where electrical discharges were common at accelerating potentials of less than 4000 V. Higher accelerating voltages are desirable because they provide higher overall instrument sensitivities. It was found that the occasional discharge that still occurred with the new arrangement often shut off the oven heater and fan in the chromatograph. This problem was solved by modifying the electronic circuitry of the chromatograph responsible for the shutdown in such a way as to maintain the circuits' original safety functions, but prevent it from responding to the electrical impulse generated by a transient breakdown in the ion source or interface probe.

The interface probe was tested to determine whether the new design, which offers intimate contact between the capillary flow restrictor and the heater surface, allowed the transport of higher-molecular-weight materials through the capillary restrictor as compared with the old design. A variety of materials were used in these testing procedures, including mixtures of polybutadiene oligomers, polyethylene glycol oligomers, and PAH from coal tar and carbon black extracts.

Isopentane was used as the mobile phase (supercritical fluid) at a temperature of 220°C and at a pressure that was typically ramped from 24 or 30 atm to between 50 and 70 atm at rates ranging from 0.2 to 5 atm/min. Short chromatographic columns (< 8 m) were used to effect some separation between the analytes and the solvent, but little effort was made to optimize the chromatographic separations. The temperature of the probe tip was varied between 220°C and 550°C in attempts to determine the optimum temperature for each material and flow rate, but frequent restrictor plugging made the reproducible conditions required for such comparisons very difficult to achieve. It was noted, however, that higher-molecular-weight materials were observed in the analyses using this new design as compared to the interface probe design. For example, the highest molecular weight material observed for the analysis of PAH from carbon black using the older design had a molecular weight less than 300 daltons, whereas PAH with molecular weights in excess of 400 daltons were observed in the analysis using the new interface probe.

In order to assess the degree of discrimination that might still be occurring with the new interface, the carbon black extract was analyzed by direct probe mass spectrometry, a technique that is relatively free of mass discrimination for the compounds present in the extract. The direct probe analysis was performed using chemical ionization, with isopentane as the chemical ionization reagent gas, so as to eliminate differences in the spectra that might occur if different ionization modes were used in the two analyses. The individual mass spectra that were acquired over the desorption period in the direct probe analysis were summed together to create an averaged spectrum that accurately represents the composition of the carbon black extract (shown in Figure 4A). In a similar manner, the individual mass spectra acquired during the elution of the separated components of the carbon black extract during an SFC/MS analysis were summed together to produce an average mass spectrum (depicted in Figure 4B). Comparison of these indicates the continued presence of discrimination against higher mass components in the SFC/MS results. The amount of discrimination, however, is decidedly less than was present with the old interface, but future efforts still need to address the origin of this discrimination.

INSTRUMENT CALIBRATION

A vital component in the operation of high resolution, high mass, mass spectrometer systems is the mass calibration standard. Because the SFC-MS instrument is operated with chemical ionization (CI), appropriate calibration

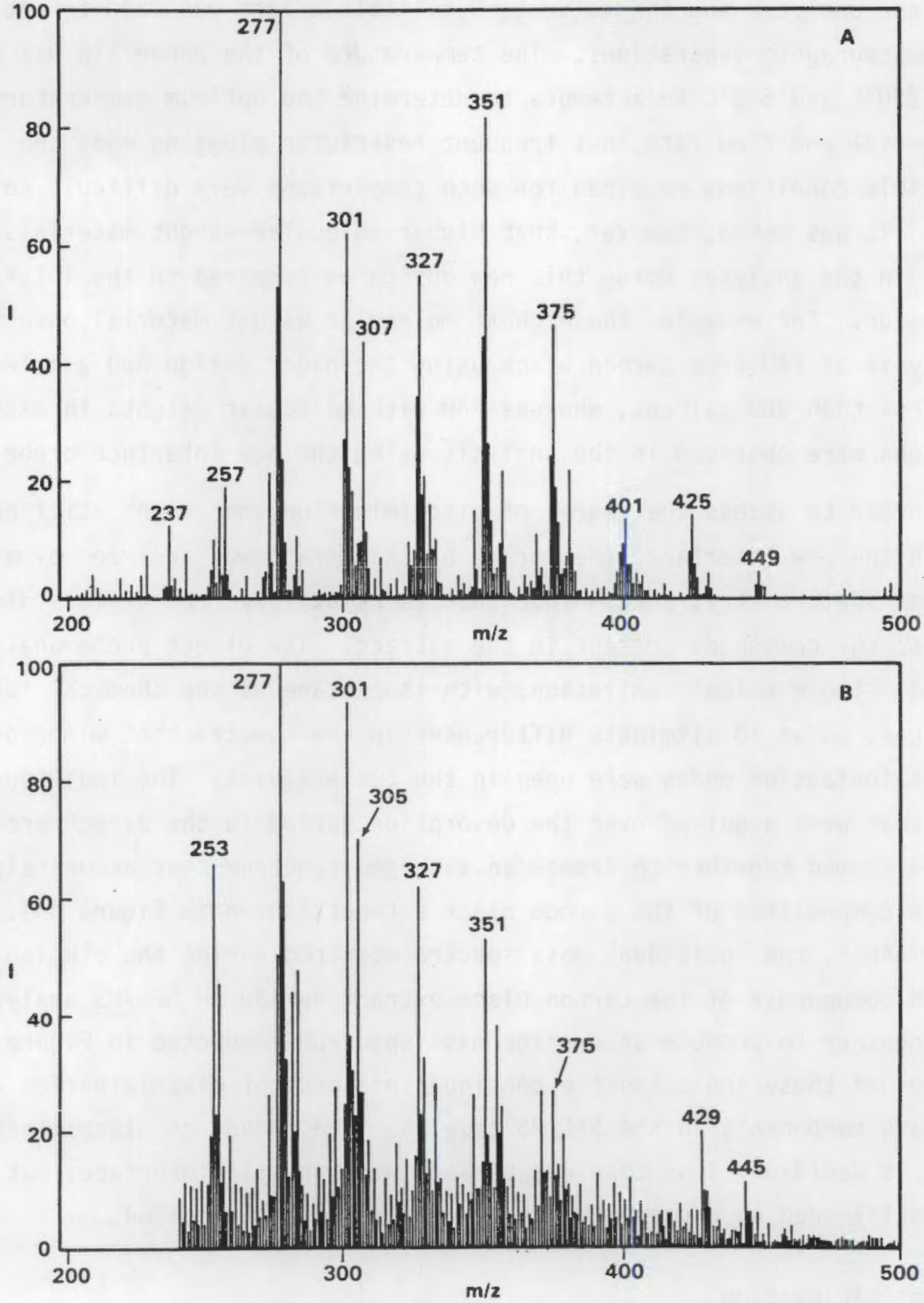

FIGURE 4. Averaged Mass Spectra of Carbon Black Extract Acquired Using Isopentane CI by (A) Direct Probe and (B) SFC/MS

standards for use in CI needed to be established. Mass calibration standards typically used in electron impact (EI) ionization do not generally perform well in CI. And, as improvements to the direct fluid injection (DFI) interface have been made, it has become necessary to identify standards and introduction modes that permit calibration in excess of 1000 dalton. Mixtures of polyethylene glycol (PEG) oligomers have been utilized. These mixtures are introduced using a small glass capillary inserted into the ion source on the end of a direct insertion probe. This method of introduction has been sufficient for early experiments but has been limited to about 1000 daltons for positive ion chemical ionization.

Experimental work with polyethylene glycol oligomers is continuing with ammonia utilized as the CI reagent gas. Chemical ionization with ammonia is a low energy process that results in mass spectra containing molecular adducts with ammonium ions, $(M+NH_4)+$, for materials with proton affinities lower than ammonia (PA = 205 kcal/mole), and little fragmentation of analytes. Using ammonia as the CI reagent gas and the direct insertion probe for calibrant introduction, the mass spectrometer can now be calibrated, in the SFC-MS mode, to about 1400 dalton. Work will continue using PEG as a calibration mixture, and using new methods of calibrant introduction, in an effort to extend the calibration to 2000 daltons.

IMPROVEMENTS TO THE SOLVENT DELIVERY SYSTEM

The quality of chromatographic performance of a supercritical fluid chromatograph depends in part upon the ability to control the pressure and temperature (density) of the supercritical fluid used as the mobile phase in SFC. Earlier instrumentation used a relatively simple analog controller to determine the syringe pump pressure. Although this controller generated a signal that caused a smooth pressure change to occur, it was very difficult to set the rate of change to a specific value. In order to eliminate this difficulty, an Apple IIe® computer (Apple Computer Inc., Cupertino, California), with a disk drive and an Adalab® (Interactive Microware Inc., State College, Pennsylvania) interface card, and a newly designed digital syringe pump control unit, compatible with the new computer, were interfaced to the high pressure syringe pump. Software allowing pressure or density programming of the fluid was written (in BASIC and FORTH languages) and installed in the data system. The digital pump controller and software were developed in our laboratory in conjunction with other programs involving the development of SFC, and this technology was tested and improved using other SFC systems before being installed on this SFC/MS system. This new computerized pump controller not only allows great flexibility in pressure and density programming, but provides more stringent control of the pump pressure and a record of the actual fluid pressure throughout the chromatographic period. Analysis of this recorded pressure data indicated that the fluid pressure was maintained during the chromatographic analysis within ±1 bar of the programmed value at all times.

When the new computerized pump controller was used in the acquisition of SFC/MS data, a marked improvement in chromatographic performance over the old system was evident. Figure 5 details the reconstructed total ion current chromatogram and selected single ion chromatograms for the protonated molecular ions of major components in a coal tar chromatographed using supercritical isopentane at 220°C and an 8.1 m x 50-μm-ID DB-1 fused silica capillary column (J&W Scientific, Folsom, California) with the following chromatographic program: an initial pressure of 30 bar held for 2 min, followed by a linear pressure ramp at 5 bar/min to 70 bar, a 10-min hold at 70 bar and then a linear pressure ramp of -11 bar/min back to the initial conditions. The major components include the polycyclic aromatic hydrocarbons naphthalene (m/z 129), methylnaphthalenes (m/z 143), dimethylnaphthalenes (m/z 157), fluorene (m/z 167), anthracene and phenanthrene (m/z 179), pyrene and fluoranthenes (m/z 203), chrysene (m/z 229), and benzopyrenes and perylene (m/z 253). Although these results indicate that improvements are still needed in chromatographic performance, the results also mark the first reasonably good chromatography that was achieved with this SFC/MS instrumentation.

CHARACTERIZATION OF POLAR-MODIFIED MOBILE PHASES

The solvating power of a supercritical fluid mobile phase (to a first approximation) is directly proportional to the density and is dependent on the chemical characteristics of the fluid. Intrinsically higher solvating powers

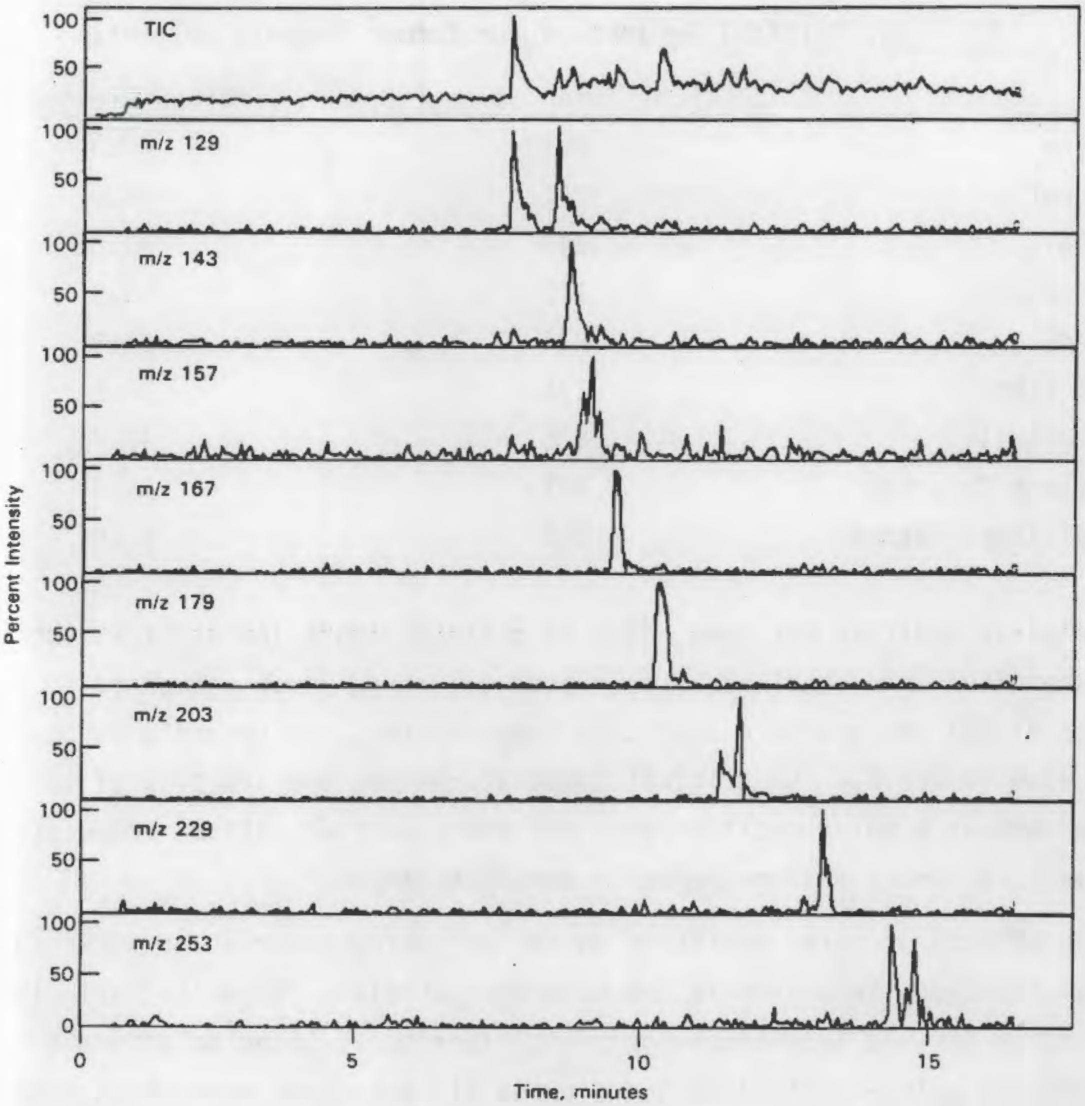

FIGURE 5. Reconstructed Total Ion and Selected Ion Chromatograms for an SFC/MS Analysis of Coal Tar

and specific chemical selectivities can be obtained by selecting fluids with specific chemical properties (e.g. presence of polar functional groups, pi bonds, etc.). Unfortunately, the critical temperatures for the more polar solvents that provide the capacity for specific or selective chemical interactions are prohibitively high (generally in excess of 250°C) to be used as supercritical fluid mobile phases (the critical parameters for a number of supercritical fluids are given in Table 1). However, mixed fluid systems, in

TABLE 1. Critical Parameters for Common Organic Solvents

Compound	Critical Temperature (°C)	Critical Pressure (atm)
Benzene	289	48.3
Methanol	241	78.9
Ethanol	243	63.0
Isopropanol	235	53.0
Acetone	235	47.0
Ethyl Ether	194	35.5
Acetonitrile	275	47.7
Methylene Chloride	237	60.0
Methyl Ethyl Ketone	262	41.0

which a polar modifier has been added to a fluid with a low critical temperature, are often characterized by increased solvating power (compared to the nonpolar fluid) and moderate operating temperatures. In general, nonpolar fluids have relatively low critical temperatures and the addition of up to 20 mole percent of a polar modifier will not increase the critical temperature of the resulting binary mixture beyond a workable range.

The effects of polar modifiers on the solvating power of nonpolar supercritical fluid mobile phases in SFC have been studied. Capacity ratio (k') measurements derived from chromatographic experiments using polar probe molecules and polar-modified carbon dioxide fluid systems have shown significant decreases in retention of the probe molecules, indicating increased mobile phase solvating power. Data for selected probe molecules and fluid systems are summarized in Table 2.

The polar modifiers used in these studies all acted to increase the solvating power of the mobile phase, with the isopropanol creating the largest decrease in retention, followed by acetonitrile and methanol (a lower value for k' in Table 2 indicates a shorter retention time for the probe molecule, indicating increased solvating power of the mobile phase). The 20 mole percent modifier concentration was sufficient to drastically change the solvating properties of the carbon dioxide, and yet the critical temperatures were

TABLE 2. Capacity Ratio Data(a)

Compound	k'			
	CO_2	CO_2-CH_3CN(b)	CO_2-CH_3OH(b)	CO_2-Isopropanol(b)
Decylbenzene	0.97	0.09	0.13	0.05
Myristophenone	4.99	0.15	0.21	0.13
Phenanthrene	4.86	0.32	0.57	0.25
Phenanthridine	6.09	0.33	0.44	0.26
Phenalen-1-one	8.65	0.35	0.51	0.29

(a) Chromatographic conditions: 120°C and 168 atmospheres.
(b) 20 mole percent modifier mixture.

maintained below 120C. Considering the magnitude of the retention decreases, it is probable that modifier concentrations lower than 20 mole percent would be used in most separations.

Capillary SFC/MS chromatograms obtained with a quadrupole mass spectrometer of coal tar mixture using an isopropanol modified propane (10% v/v) fluid system are shown in Figure 6. These chromatograms were obtained at different chromatographic operating temperatures and illustrate the importance of understanding the phase behavior of binary fluid mixtures. The separation obtained at 120°C shows very poor separation efficiency, with the components being eluted in an unresolved hump at lower pressures. Increasing the temperature by 10°C (to 130°C) dramatically improved the chromatographic performance, producing much narrower peaks and eluting the components over a wider pressure range. At the lower temperature, the fluid mixture was probably below its critical point and a subcritical liquid existed as the mobile phase. Increasing the temperature another 20°C to 150°C only slightly improved the chromatographic performance. This example not only illustrates the importance of understanding the critical phase behavior of a fluid mixture, but demonstrates the improved chromatographic performance of a supercritical mobile phase compared to a subcritical liquid mobile phase where pressure programming advantages are minimal. The use of a polar modified fluid for the SFC/MS

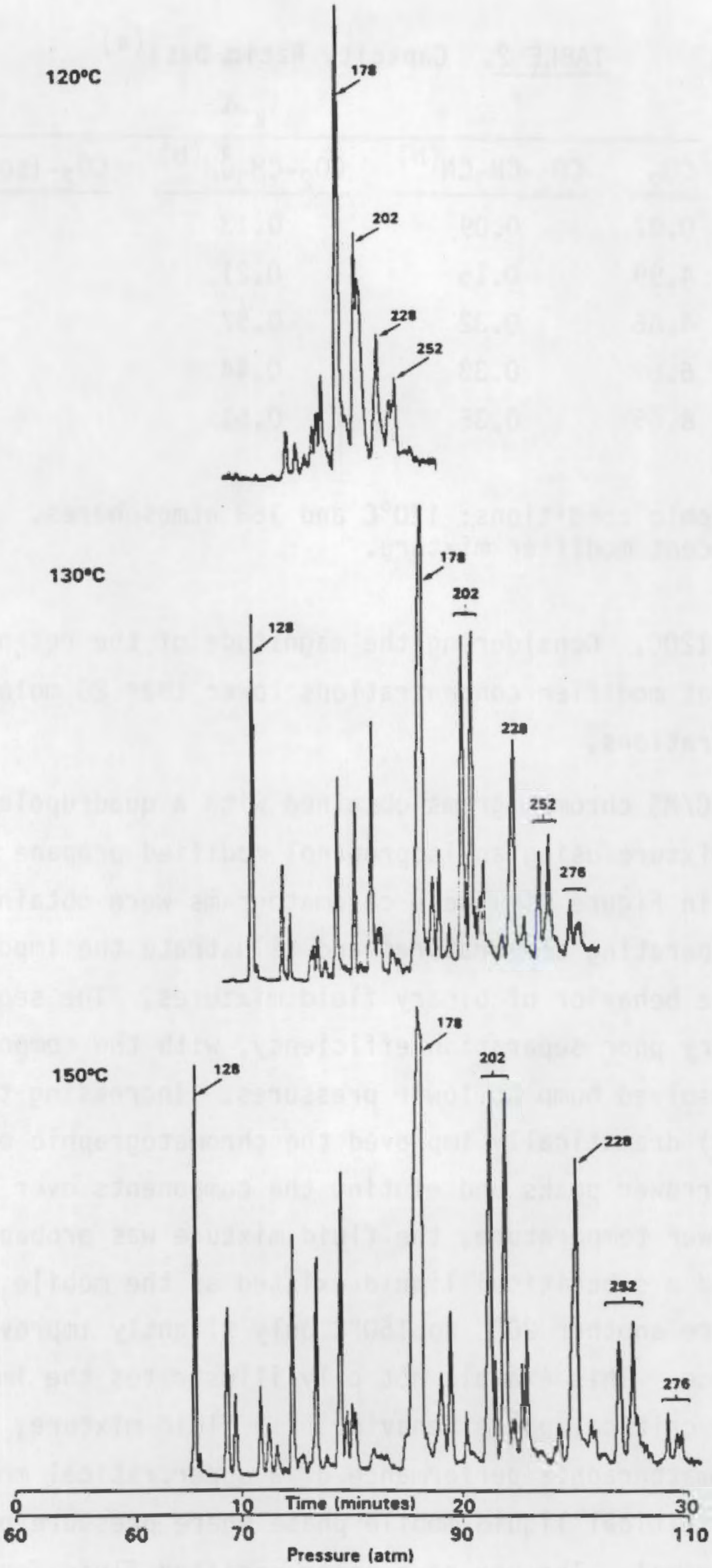

FIGURE 6. Capillary SFC/MS Chromatograms of Coal Tar Obtained at Different Temperatures Using a Polar Modified Mobile Phase

(quadrupole) analysis of a moderately polar polymer mixture (polyethylene glycol) is shown in Figure 7. This separation was obtained at 125°C using an isopropanol-modified carbon dioxide fluid system (5% v/v) and a 10 m x 50-m-ID capillary column coated with a crosslinked and surface bonded 5% phenyl polymethylphenylsiloxane stationary phase. The mobile phase pressure was ramped from 140 to 210 bar at 2.5 bar/min. The oligomer distribution obtained by SFC/MS corresponds to the specified average molecular weight of the polymer sample.

USE OF POLAR-MODIFIED FLUIDS WITH THE MAGNETIC SECTOR MASS SPECTROMETER

We have shown that supercritical pentane is a good solvent for high-molecular-weight PAH and polymeric materials, such as polystyrene and polybutadiene, which are thermally stable, and relatively nonpolar and nonvolatile, but have limited solubility in conventional organic solvents. These experiments also demonstrated that the SFC/MS instrumentation designed and constructed for this program functions under the relatively demanding conditions required for supercritical pentane (i.e., high temperature). Achieving the next major milestones of the program has involved developing the methodologies to use more polar fluids for the analysis of polar compounds. The progress achieved in developing these methodologies will be discussed in three separate areas: results from research using 1) direct fluid injection (DFI), 2) supercritical fluid chromatography (SFC) introduction, and 3) supercritical fluid extraction (SFE) and introduction of supercritical fluids into the mass spectrometer.

Direct Fluid Injection-Mass Spectrometry

Polar-modified carbon dioxide fluids (mixtures of CO_2 and isopropanol) were used to evaluate the operating parameters of the supercritical direct fluid injection-magnetic sector mass spectrometer system. The evaluation was performed to determine conditions required for efficient transfer of higher molecular weight polar materials to the ion source. Polyethylene glycol mixtures are ideal for use in studies to determine the sources of discrimination against higher molecular weight materials in the DFI-MS interface because they are commercially available in relatively well characterized, high purity

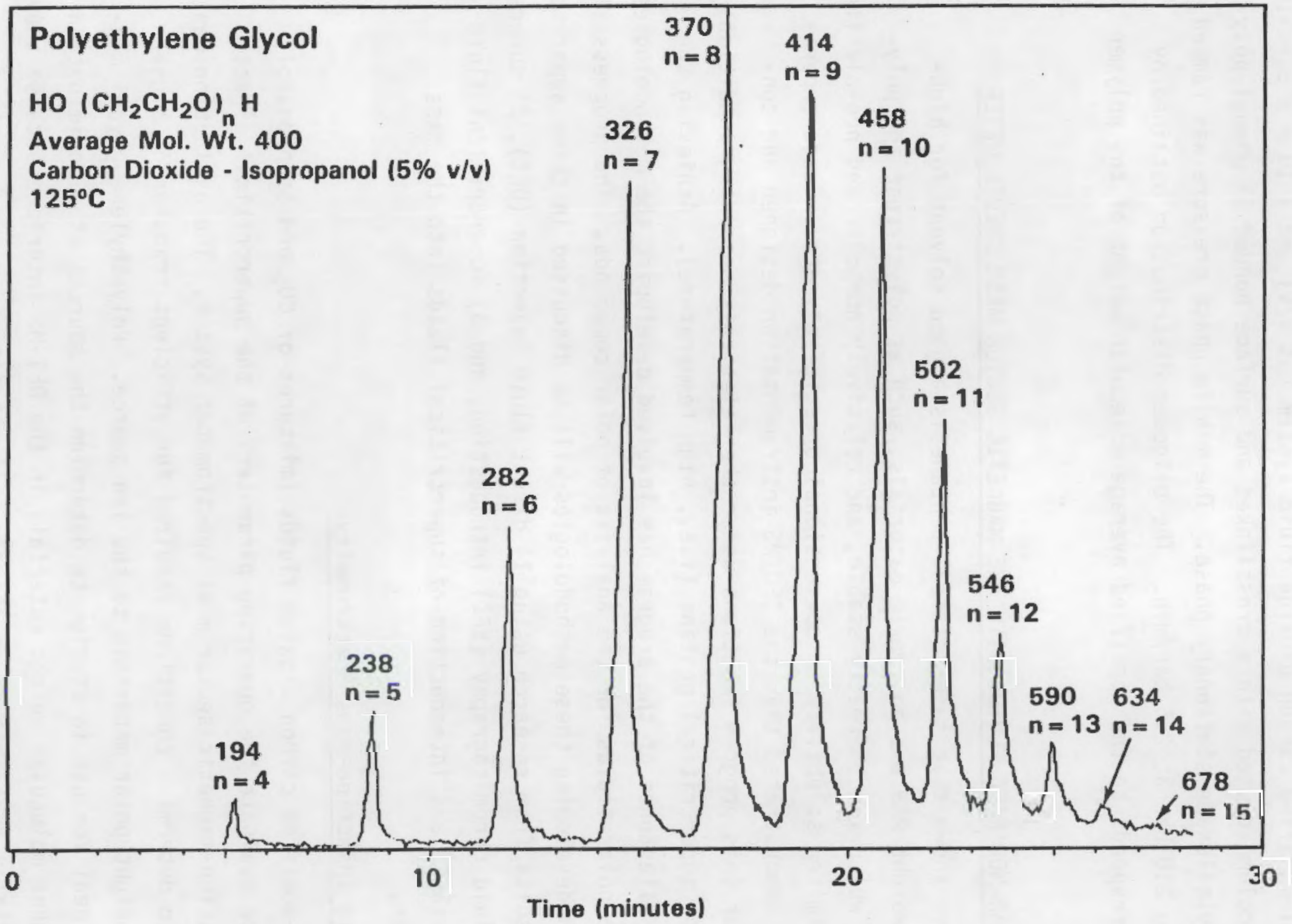

FIGURE 7. Capillary SFC/MS Chromatogram of a Polyethylene Glycol Polymer Mixture Obtained with a Polar Modified Mobile Phase

formulations with mass ranges appropriate for these studies. The ammonia CI mass spectra of a 600 AMW PEG sample introduced using a quartz capillary on the direct insertion probe and via direct fluid injection are depicted in Figures 8A and 8B, respectively. A short length (1 m) of 50 μm ID capillary column, coated with an SE-54-like stationary phase, was used to transport the PEG sample to the interface for DFI-MS with no effort made to chromatographically separate the sample. A 5% (v/v) mixture of isopropanol in carbon dioxide was used as the supercritical solvent for DFI. The spectrum obtained following direct probe introduction resulted from materials that were able to be volatilized at the temperature of the probe tip (the probe tip has no facility for heating, and is likely at a temperature slightly less than source temperature). The ion at m/z 916 corresponds to the n=20 oligomer (nominal m.w. 898) and numerous lower molecular weight ions are present due to fragmentation of higher molecular weight oligomers. Reasons for the apparently high amount of fragmentation, especially under ammonia CI conditions, are not readily discernible. The use of supercritical DFI is found to be effective for transporting this sample to the ion source as evidenced by the constant presence of m/z 872 ion (n=18 oligomer) and the intermittent detection of the m/z 916 ion at about 1% relative abundance. Much of the abundant fragmentation in this spectrum is likely due to thermal degradation (pyrolysis) of the sample in the DFI interface at the relatively high (390°C) restrictor heater temperatures. Parameters controlling effective transport of less volatile and more thermally labile materials through the DFI interface, such as the restrictor heater temperature, the capillary flow restrictor geometry, and the supercritical fluid velocity through the flow restrictor, remain to be studied in detail. Also to be addressed is the utility of pyrolysis-mass spectrometry for the characterization of nonvolatile materials following SFC.

Supercritical Fluid Chromatography-Mass Spectrometry

The first polar modified fluid chosen to be investigated in this program for use with SFC/MS was 5% isopropanol in carbon dioxide (5% by volume). An 8-meter, 50-μm-ID SE-54 type column was installed in the supercritical fluid chromatograph and analyses made of simple test solutions containing aromatic compounds using various conditions for pressure and temperatures. The simple

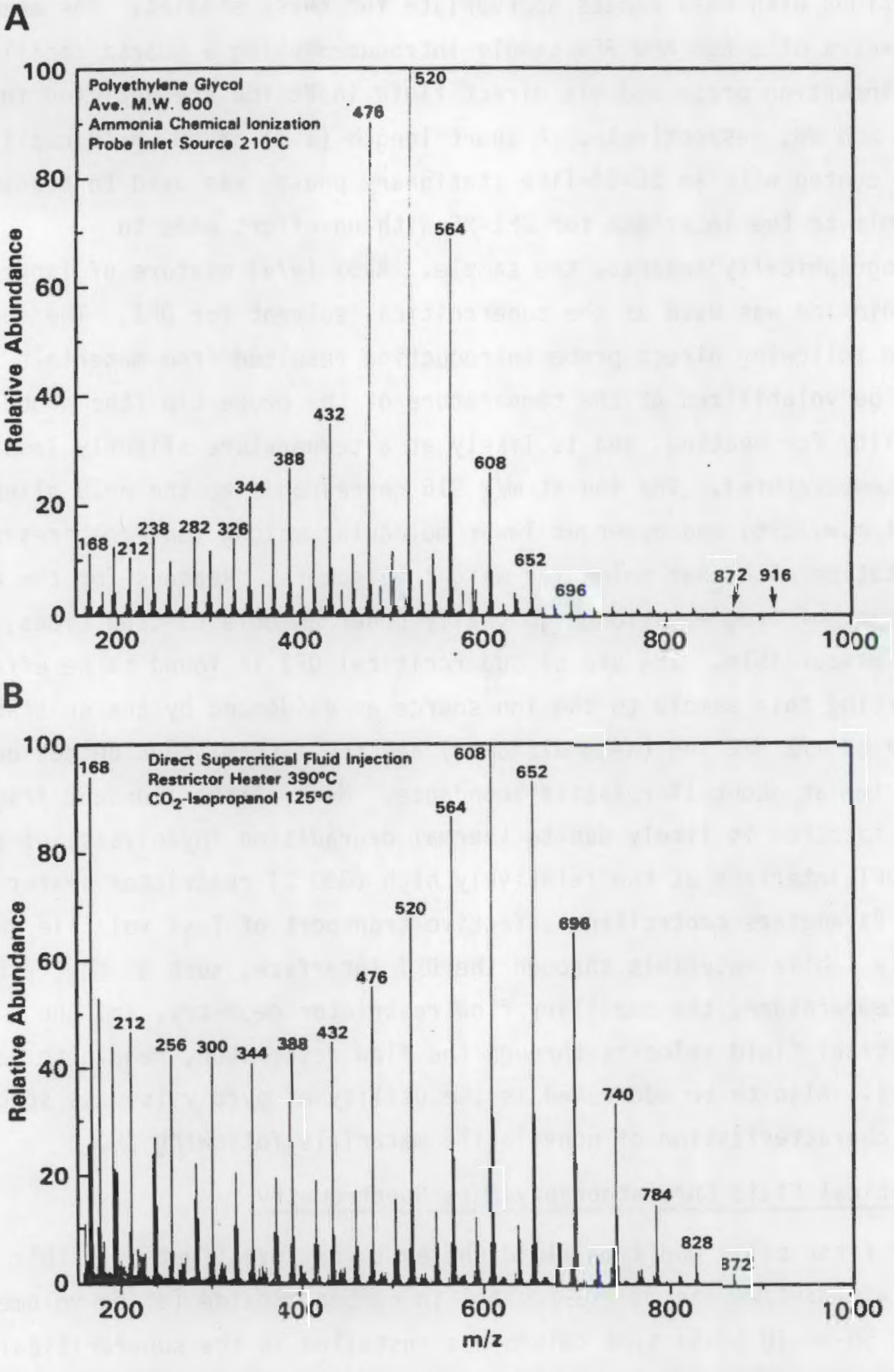

FIGURE 8. Mass Spectra of a Polyethylene Glycol Polymer Mixture Acquired Using Ammonia CI by (A) Direct Probe and (B) DFI/MS

test solutions consisted of single components, such as O-dichlorobenzene, or mixtures of aromatic compounds, such as decylbenzene, phenanthrene, bibenzyl, phenanthridine, and myristophenone, in a solvent such as benzene or dichloromethane. A coal tar standard was also investigated using the mixed fluid system. Results from these initial experiments using 5% isopropanol/CO_2 demonstrated that the design of the interface probe was suitable for operation with fluids more polar than pentane. The background ions observed in mass spectra acquired using isopropanol/CO_2 as the supercritical fluid and chemical ionization reagent ion system were reduced in both intensity and distribution throughout the spectra as compared to the mass spectral background ions arising from pentane or isopentane chemical ionization, resulting in "cleaner," more easily interpretable spectra. In addition, the isopropanol/CO_2 chemical ionization reagent system led to less fragmentation and greater production of protonated molecular ions for PAH compared to the pentane or isopentane chemical ionization reagent system. Adduct ions resulting from the addition of $C_3H_7^+$ to the neutral PAH molecule have been observed for some PAH, although it is presently not clear why the adduct ions form only for certain PAH.

The general appearance of the SFC/MS chromatograms for data acquired with the isopropanol/CO_2 fluid demonstrated that reasonably good chromatography is feasible, exhibiting high resolution and efficient transfer of materials into the ion source. The total ion chromatogram of the isopropanol/CO_2 SFC/MS separation of an aromatic fraction of a coal tar extract is shown in Figure 9. Chromatography was performed at 125°C from 130 bar using a 5 bar/min pressure ramp. This is an example of preliminary experiments using a polar modified fluid in this SFC/MS system and efforts to achieve optimum chromatographic performance had not been made. However, the efficiency of the separation is exemplified by the narrow peak widths (20 sec full-width at half height, for the m/z 179 event) and by the separation of various C_2-naphthalene isomers (m/z 157). For this separation, the restrictor heater was operated at approximately source temperature (220°C) and the highest molecular weight components known to be in this fraction (molecular weight 276) were detected. Optimization of chromatographic conditions, such as pressure ramp rate and column temperature, and a study of the effect of restrictor heater temperature

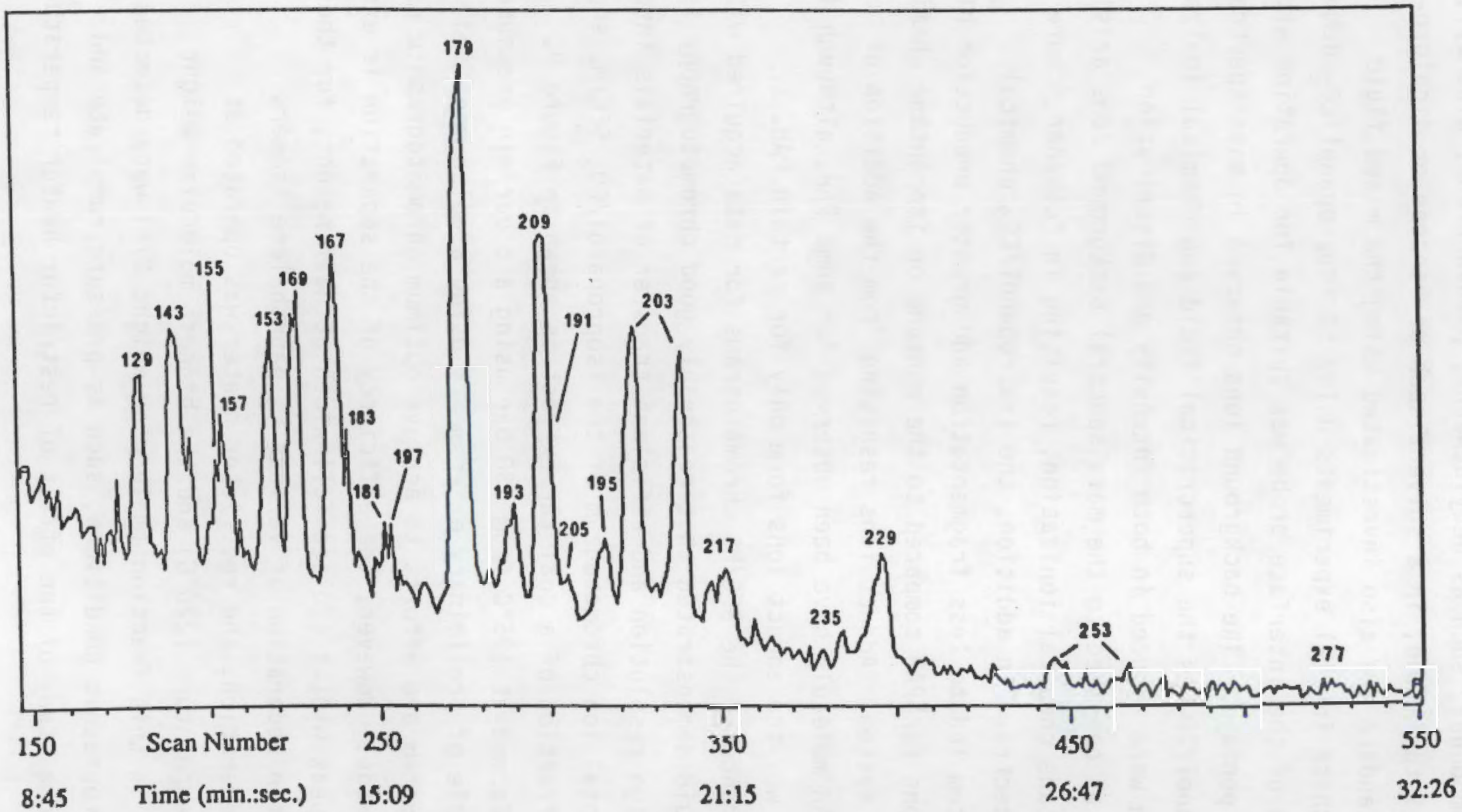

FIGURE 9. Total Ion Chromatogram of the SFC/MS Analysis of a Coal Tar Extract Using 5% Isopropanol/CO_2 Mobile Phase (The nominal masses of the protonated molecular ions of some components are detailed on the chromatogram)

should lead to improved analysis of this type of sample. However, even without this optimization, this separation showed more effective separation and detection, with a better signal-to-noise ratio, than the previous efforts using this instrumentation with supercritical isopentane (compare Figure 9 with Figure 5).

A 5% (v/v) isopropanol-carbon dioxide supercritical solvent was used to analyze 400 and 600 AMW polyethylene glycol samples with the high resolution mass spectrometer system. Ammonia and methane CI mass spectra of oligomers from these samples were obtained following SFC introduction into the ion source. Figure 10 shows the ammonia (A) and methane (B) CI mass spectra of the n = 12 oligomer of polyethylene glycol (MW = 546). The ammonia CI spectrum is characterized by an abundant ammonium adduct ion at m/z 564 and fragment ions separated by 44 daltons corresponding to ions of the structure $[H\text{-}(OCH_2CH_2)\ n\text{-}OH] + NH_4^+$ formed by cleavage of carbon-oxygen bonds along the polymer chain. Smaller ions corresponding to the protonated molecule at m/z 547 and other less abundant fragments are also present. The more energetic methane chemical ionization leads to spectra characterized by low abundance protonated molecules, in this instance at m/z 547, and a greater abundance of low molecular weight fragments. One reason for choosing the n=12 oligomer for this comparison is that the protonated molecular ions from methane CI for the larger oligomers were either of very low abundance (<5%) or not detected.

Supercritical Fluid Extraction-High Resolution Mass Spectrometry

The ability to obtain exact mass information adds an extremely valuable tool for the characterization of an unknown material. The direct fluid injection (DFI) interface has been used with SFC as well as supercritical fluid extraction (SFE) to obtain mass spectral data on unknown samples. Recent work (Kalinoski et al. 1986) has demonstrated the utility of DFI-MS for the characterization of supercritical fluid extracts of complex natural materials. High resolution mass spectrometry interfaced with SFE enabled exact mass (±3 ppm) information for two polar fungal toxins present in a wheat sample to be obtained. Coupled with previous work, a detection limit of around 10 ppb appears feasible for this method. Figure 11 is an oscillographic trace of the ammonium adduct ion region (m/z 384) of the trichothecene mycotoxin diacetoxy

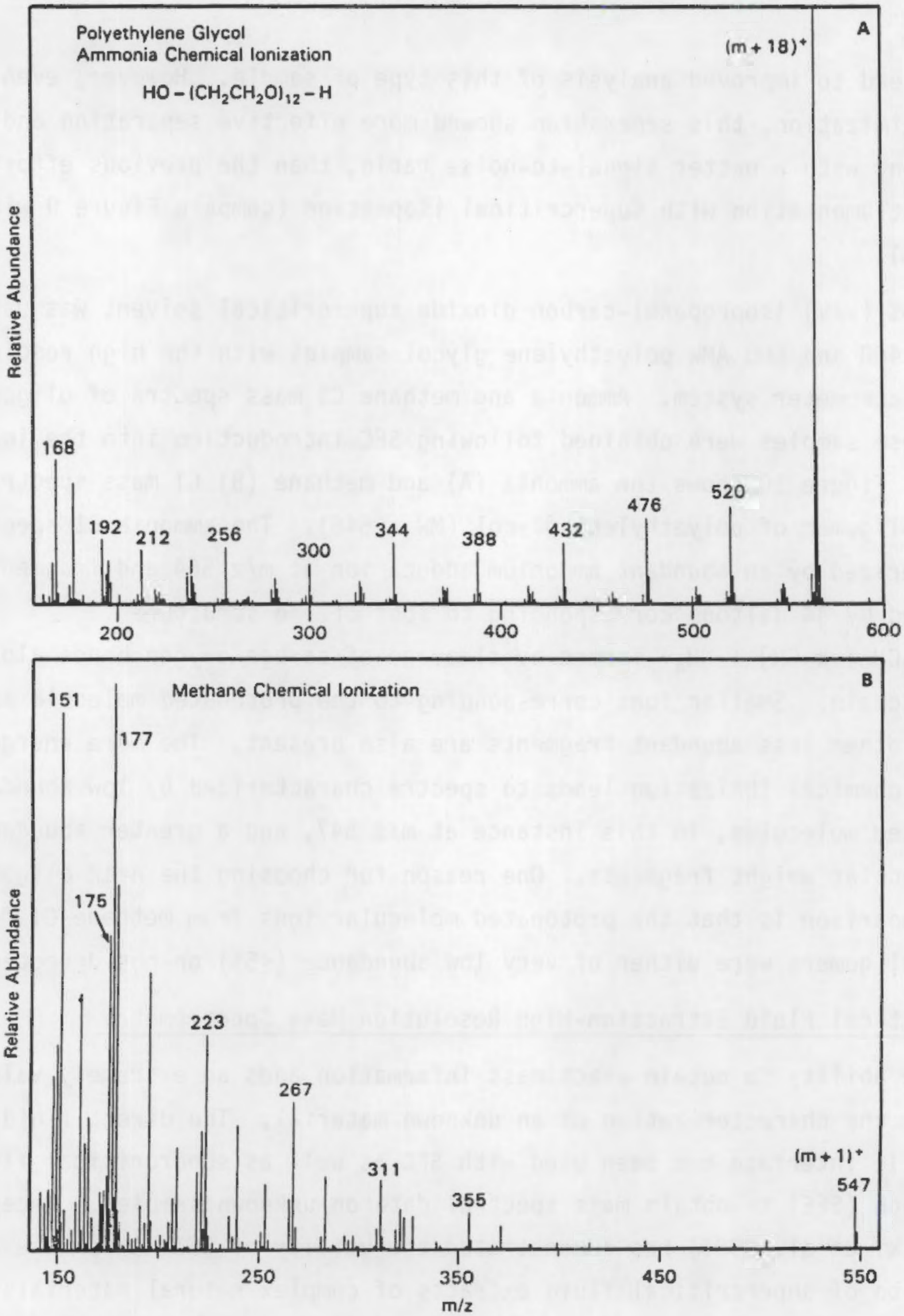

FIGURE 10. Mass Spectra of the n=12 Oligomer of Polyethylene Glycol Acquired by SFC/MS Using (A) Ammonia CI and (B) Methane CI

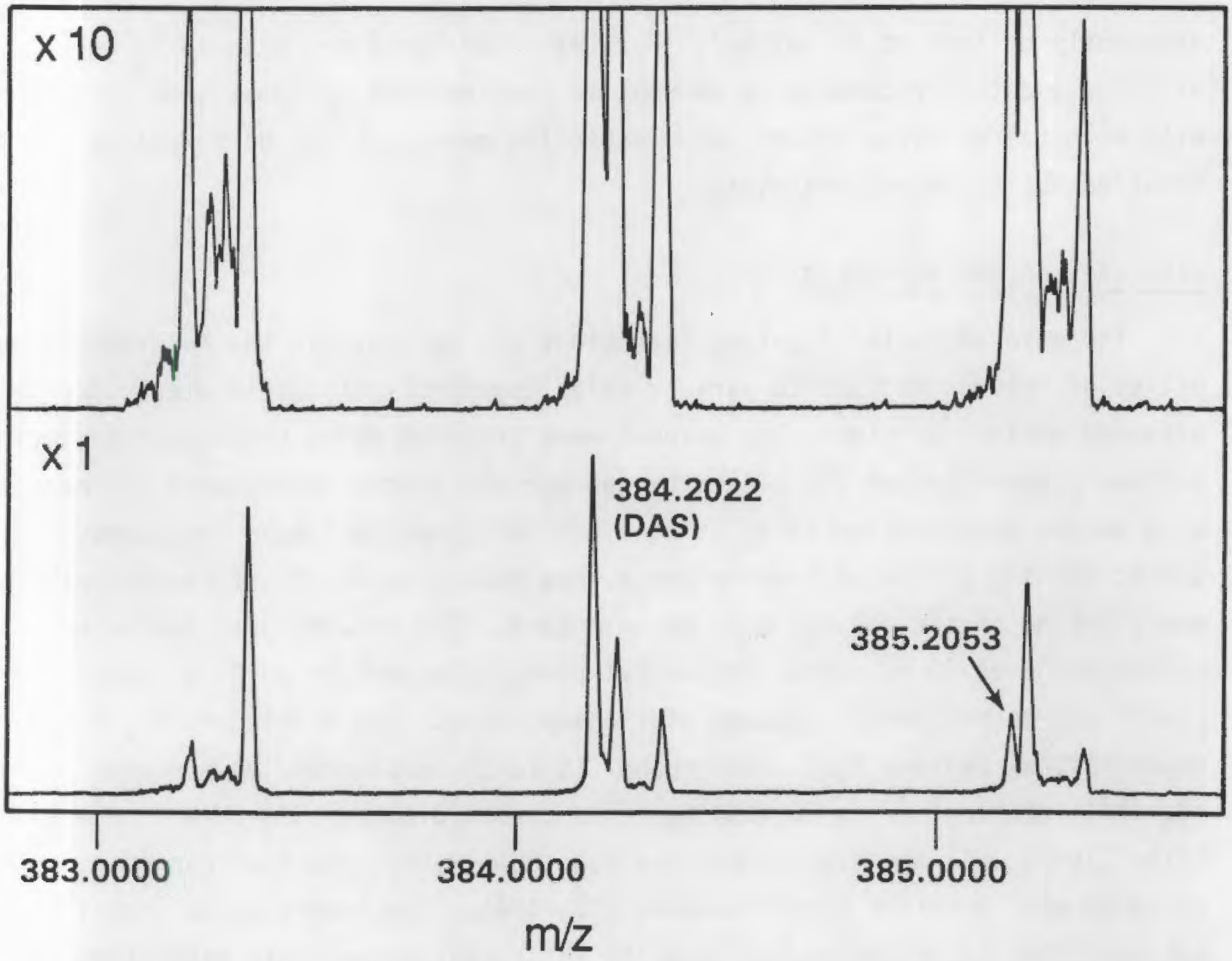

FIGURE 11. Partial High Resolution Mass Spectrum of the Molecular Ion Region for Diacetoxyscirpenol Extracted from Wheat Using a Supercritical Fluid Mixture of CO_2-Isopropanol (5% v/v, 120C, 240 bar; mass resolution, 1:7,400)

scirpenol (DAS, nominal m.w. 366). An extraction cell had been filled with wheat spiked with DAS and T-2 toxin (nominal m.w. 466) and extracted with a supercritical mixture of CO_2 and isopropanol (5% v/v). The total effluent of the extraction cell was transported to the mass spectrometer ion source for ammonia CI mass spectrometry. Comparison of ions in the mass spectrum with the calculated exact molecular weight of the DAS-ammonium adduct ion allowed DAS to be identified in the presence of numerous isobaric interferences. This same procedure was used to identify T-2 toxin in the same extract. The instrument has been operated in an SFE-MS mode at resolution up to 20,000 (m/4m, defined rigorously defined at 5% valley). Further experiments are planned in which exact mass data for components present in complex fuel and coal product samples will be obtained using SFE-MS, and resolution mass spectral data will be obtained during SFC-MS analyses.

CAPILLARY COLUMN TECHNOLOGY

The main emphasis of column technology was to evaluate the long-term stability of columns exposed to various polar supercritical mobile phases for extended periods of time. The columns were prepared using techniques including surface preparation of the silica by appropriate thermal treatments, formation of a bonded deactivation layer using a polymethylhydrosiloxane treatment, static coating of the stationary phase, and extensive in situ free-radical crosslinking of the polymer with azo-*t*-butane. The columns were coated with either an SE-54 (a 5% phenyl polymethyl-phenylsiloxane) or an OV-17 (a 50% phenyl polymethylphenylsiloxane) stationary phase. The mobile phases included supercritical pentane (C_5), isopropanol (5 to 10 vol%) modified pentane (C_5-IPA), methanol (2 to 20 wt%) modified carbon dioxide (CO_2-CH_3OH), acetonitrile (10-20 wt%) modified carbon dioxide (CO_2-CH_3CN), and isopropanol (2 to 20 wt%) modified carbon dioxide (CO_2-IPA). Stationary phase stability was monitored by measuring the capacity ratio (chromatographic retention factor, k') of selected compounds under a specific set of chromatographic operating conditions before and after exposure to the various supercritical fluids. The capacity ratio magnitude is directly proportional to the amount of stationary phase in the column. Capacity ratios were measured under both gas and supercritical fluid chromatographic conditions. Some of these data are summarized in Table 3.

The larger capacity ratios for the last two columns were obtained by gas chromatography as opposed to supercritical fluid chromatography for the first three columns. In general, it can be observed that the capacity ratios for all but one of the columns did not change significantly after long-term use with the various polar supercritical fluids. This behavior indicates that the stationary phase was adequately stabilized on the column surfaces and was not

TABLE 3. Stationary Phase Stability Summary

		Capacity Ratios (k')									
	(Compound)	A		B		C		D		E	
Column	Fluid Exposure	Before	After	Before	After	Before	After	Before	After	Before	After
OV-17	CO_2-CH_3OH[a,b]	0.96	0.99	4.87	4.86	5.19	4.79				
OV-17	CO_2-CH_3CN[a,c]	0.99	0.94	4.87	5.02	4.79	5.83				
OV-17	CO_2-IPA[a,d]	0.94	1.04	5.02	4.97	5.83	5.89				
SE-54	C5&C5-IPA[e]							17.5	15.7	38.3	39.1
SE-54	C5&C5-IPA[e]							6.1	2.0	12.0	4.4

(a) 120°C and 2500 psi(Compound)A: n-decylbenzene
(b) 15.4 wt% CH_3OHB: phenanthrene
(c) 18.9 wt% CH_3CNC: myristophenone
(d) 25.4 wt% IPA (Isopropanol)D: n-decane
(e) 210-230C, 400-1000 psi, 5 vol% IPAE: n-undecane

being stripped by the supercritical mobile phases. However, the chromatographic column listed last in Table 3 displayed a fairly significant decrease in capacity ratios, indicating that a large portion of the stationary phase had been stripped from the column. Both of the SE-54 columns were used for several months under rather demanding conditions of pressure programming. The only difference in preparation procedures for the two SE-54 columns was that the more stable column was initially coated with a film of stationary phase that was approximately three times thicker than the column that lost its stationary phase. This may account for the greater stability, although differences in silica surface modification procedures, deactivation methods, and crosslinking techniques would be expected to have greater impact.

Some experiments to optimize the chromatographic parameters using supercritical isopentane were unable to be completed due to deterioration of the chromatographic column. Desired optimized conditions were not achieved because the capillary flow restrictor would plug as the pressure exceeded 50 bar for each analysis. It was also noted that the separations between individual mixture components that eluted soon after the solvent peak were becoming smaller with each analysis. These observations indicated that the efficiency of the chromatographic column was decreasing rapidly due to some form of modification of the stationary phase of the column. When the column was removed from the supercritical fluid chromatograph and evaluated by gas chromatography, it was found that almost all the stationary phase had been stripped from the column by the isopentane. This stripping process undoubtedly supplied much of the material that plugged the capillary restrictors. These results were noted for a number of columns prepared during a common time period. It was determined that a cross-linking reagent, azo-*t*-butane, had been contaminated and columns were not properly prepared. Procedures have been instituted to prevent such problems in the future.

CONCLUSIONS

During FY 1986, technical progress toward the programmatic goals of developing and evaluating SFC/MS for the analysis of higher-molecular-weight compounds was made in the following areas:

- Studies have been conducted to characterize the requirements for and to facilitate the transfer of thermal energy to the capillary flow restrictor region. Such studies have resulted in a new interface probe design.
- The redesigned interface probe was constructed and tested. The new design was shown to allow better transport of higher molecular weight, less volatile compounds than the previous design, decreasing the mass discrimination occurring at the SFC-MS interface region.
- Methods allowing the mass calibration of the magnetic sector mass spectrometer to 1400 daltons have been developed.
- A digital syringe pump controller, interfaced to an Apple IIe computer, has replaced the previous analog pump control unit, allowing much finer and more reproducible control of the pressure (density) of the supercritical fluid mobile phase.
- Relatively nonpolar supercritical fluid mobile phases have been modified by the addition of small amounts of polar fluids to create fluids with higher solvating powers than, but with similar operating parameter to, the non-modified fluids. Results from characterization experiments indicate an in-depth knowledge of the modified fluid behavior is required for successful utilization of these modified fluids.
- Polar-modified fluids have been used with the magnetic sector mass spectrometer in experiments using three types of supercritical fluid introduction to the mass spectrometer: direct fluid injection, supercritical fluid chromatography, and supercritical fluid extraction with high mass resolution.

- Capillary columns were exposed to various polar-modified mobile phases and evaluated for stability. The test results indicated that our present methods for preparing columns are sufficient, for many of the stationary phase and supercritical fluid combinations tested, to create columns that can be successfully used with supercritical fluid chromatography.

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