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Development and Evaluation of Supercritical Fluid Chromatography/Mass Spectrometry for Polar and High-Molecular-Weight Coal Components

Technical Progress Report for the period October 1, 1986 to September 30, 1987

E. K. Chess
H. T. Kalinoski
R. D. Smith

February 1988

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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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 1987, 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 performance of the supercritical fluid chromatograph-mass spectrometer interface, and several modifications have been made to the probe, ion source, and associated hardware to improve performance and operator safety.

- Methods have been developed that allow the mass calibration of the magnetic sector mass spectrometer to 1400 daltons using desorption chemical ionization.

- The properties and range of utilities of polar and polar-modified, mixed fluids have been investigated with the magnetic sector mass spectrometer and with two types of quadrupole mass spectrometers. The polar fluids included ammonia and methylamine; the polar-modified fluids included carbon dioxide modified by the addition of small percentages of 2-propanol and acetic acid.

- Methodologies have been improved for fabricating capillary columns with bonded, crosslinked stationary phases that are suitable for use with polar fluids.

- Coal-derived materials and fossil-fuel-derived sediments have been investigated with supercritical fluid chromatograph/mass spectrometry and supercritical fluid extraction/mass spectrometry. Microbore packed columns coupled to a modified mass spectrometer interface allowed the chemical class fractionation of relatively polar complex mixtures derived from coal liquefaction.

LIST OF ABBREVIATIONS

amu	atomic mass unit(s)
AMW	average molecular weight
CCRITSL	close-coupled, reconfigured, integrated two-stage liquefaction
CI	chemical ionization
CO_2	carbon dioxide
DCI	desorption chemical ionization
DFI	direct fluid injection
DFI/MS	direct fluid injection/mass spectrometry
EI	electron impact ionization
HFR	high-flow-rate (interface)
HPLC	high-performance liquid chromatography
ID	inside diameter
MS	mass spectrometry
OD	outside diameter
NPAC	nitrogen-containing polycyclic aromatic hydrocarbon
PEG	polyethylene glycol
SFC	supercritical fluid chromatography
SFC/MS	supercritical fluid chromatography/mass spectrometry
SFE	supercritical fluid extraction
ZDV	zero-dead-volume (seal)

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STATEMENT OF ORIGINAL OBJECTIVE

The Development and Evaluation of Supercritical Fluid Chromatography/ Mass Spectrometry for Polar and High-Molecular-Weight Coal Components program, funded through the U.S. Department of Energy's Morgantown Energy Technology Center, is aimed at the development of new analytical technologies for the characterization of previously intractable complex mixtures. Our specific goals are twofold: 1) to develop and evaluate a combined high-resolution, capillary column, supercritical fluid chromatograph/high-performance mass spectrometry (SFC/MS) instrument 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 the SFC/MS instrument to develop and evaluate analytical technology applicable to coal process development. 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 evaluations of quantitative instrumental approaches, of various ionization modes, and of tandem mass spectrometry techniques for analyzing individual components in complex mixtures. A long range objective is to define the range of applicability and utility of high-performance SFC/MS methods.

PROGRAM DESCRIPTION

The project can be conceived as having three distinct 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 following instrument development phases are defined here and described in the following paragraphs: 1) design and fabrication of the supercritical fluid chromatograph, SFC/MS interface, mass spectrometer 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.

As part of the instrument design and fabrication phase, information was first obtained from the successful interfacing of supercritical fluid chromatographs to quadrupole mass spectrometers. That information was used as a basis for 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 atomic mass units (amu)], high resolution capability, sensitivity for higher masses, and potential for characterization of individual components in complex mixtures by tandem mass spectrometry techniques.

The instrument evaluation phase commenced during the design and fabrication phase, and results from the evaluation were used to further modify the instrumentation in order to improve performance. The instrumentation evaluation proceeded from the analysis of relatively nonpolar compounds, such as alkanes and polynuclear aromatic hydrocarbons, using nonpolar supercritical fluids such as pentane and carbon dioxide (CO_2), to the analysis of relatively polar components of higher molecular weight using more-polar fluids, such as methanol and ammonia, and polar-modified fluids, such as 5% 2-propanol in CO_2. During this phase of the project, the instrumentation was also 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 beyond the instrument evaluation phases, for the life of the project.

After the instrumentation had been sufficiently developed, the analysis of higher-molecular-weight and polar materials from a variety of sources commenced. The sample sources included, but were not limited to: heavy-end and refractory materials from coal conversion processes, which have proved intractable by conventional analyses. Where possible, the results are being 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 Department of Energy programs. This phase will include the development of analytical methodologies for the characterization of a wide variety of materials, and will serve to define the role and limitations of the SFC/MS technologies. The resulting knowledge will be used to critically assess the role that SFC/MS and related technologies might have in on-line process monitoring, and will aid in the design of such monitoring systems.

TECHNICAL PROGRESS

The technical progress of the third full year (months 32-43) of this program, from the end of FY 1986 to the end of FY 1987, will be reviewed in this annual Technical Progress Report for FY 1987. Following an "Experimental" section, which provides details for the general types of experiments, the progress achieved is discussed in the "Results and Discussion" section. This latter section includes plans for the next quarter and an assessment of future progress.

EXPERIMENTAL

Experiments have been conducted with three types of SFC/MS instruments, a VG ZAB-2F mass spectrometer (VG Analytical, Inc., Manchester, England), an Extranuclear single quadrupole mass spectrometer (Extrel Corp., Pittsburgh, Pennsylvania), and an Extranuclear triple quadrupole tandem mass spectrometer. The ZAB-2F system has been the primary vehicle of research for this program, and was used to conduct most of the experiments aimed at improving the chromatograph-mass spectrometer interface, extending the mass range of calibration, and characterizing fossil fuels by direct fluid injection (DFI) and by SFC coupled with MS detection. The single quadrupole instrument was equipped with a high flow rate interface, and this instrument was used for experiments in which fossil fuel materials were analyzed by SFC/MS with a packed microbore column. The tandem quadrupole instrument was used in supercritical fluid extraction (SFE) experiments.

A VG ZAB-2F mass spectrometer, equipped with an ion source modified for supercritical fluid introduction and interfaced to a supercritical fluid chromatograph, was operated in the chemical ionization (CI) mode for all experiments, using anhydrous ammonia (Matheson Gas Products, Inc., Newark, California) as the CI reagent gas. The mass spectrometer, ion source, supercritical fluid chromatograph, and interface designs have been previously described (Chess et al. 1987; Chess and Smith 1986). Total ion source chamber pressure, including reagent gas and effluent from the direct fluid injection

(DFI) interface, was approximately 1x10-4 torr, corresponding to a pressure of approximately 0.8 torr in the ion source volume, as later measured directly by a Baratron® capacitance manometer (MKS Instruments, Inc., Burlington, Massachusetts). Supercritical fluid flow through the DFI interface to the restrictor was maintained for all experiments, including those in which the samples were introduced by direct probe, to determine what effect the effluent would have on the ammonia CI mass spectra and to maintain the same ionization conditions for different types of sample introductions.

Samples of polyethylene glycol (PEG, Aldrich Chemical, Milwaukee, Wisconsin) of average molecular weight (AMW) 600, 1000, and 1500 were prepared at a concentration of about 0.1% by volume in dichloromethane (Burdick and Jackson Laboratories, Inc., Muskegon, Michigan). For experiments using desorption chemical ionization (DCI), 3-µL aliquots of the solutions were placed on the platinum wire of the DCI probe/emitter and the solvent allowed to evaporate at room temperature, in air, prior to insertion into the DFI/DCI ion source. The electrical current applied to the platinum wire was gradually increased until mass spectra of the PEG samples were obtained. For the PEG-600 this current was approximately 730-830 mA, and for PEG-1000 and PEG-1500 it was approximately 930 mA. In experiments using the unheated, solids inlet probe, the PEG-600 and -1000 samples were introduced into the ion source neat.

For experiments involving DFI of supercritical fluids, a 5% (v/v) mixture of 2-propanol (Burdick and Jackson) in carbon dioxide (SFC Grade, Scott Specialty Gas, Div. of Scott Environmental Technology, Inc., Plumsteadville, Pennsylvania) was prepared by charging the syringe pump with an appropriate volume of 2-propanol and filling the remainder of the pump with carbon dioxide. The CO_2 was dried and purified by passing through an activated charcoal and alumina adsorbent trap, with a 2-µm particle filter, before use. The SFC oven was maintained at 125°C (calculated to be higher than the critical temperature for this mixture), and the pressure was kept at 275 bar. A Valco C14W high-performance liquid chromatography (HPLC) injection valve (Valco, Inc., Houston, Texas), with a 0.06-µL injection volume, was used

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at ambient temperature for sample introduction. Because the samples were to be introduced directly, without the chromatographic separation afforded by a capillary SFC column, the injection volume was not split, as is the practice when high-efficiency separations are desired. Approximately 1 m of 50-µm internal diameter (ID) fused silica capillary column, coated with a 5% phenyl polymethylphenylsiloxane (SE-54 type) stationary phase, was used as a short transfer line. This length of coated capillary column allowed the separation of the injection solvent from the analytes, but did not afford extensive separation among the analyte species. Either a 7-cm length of 6-µm-ID fused silica capillary tubing or a comparable length of 25-µm-ID tapered tubing, drawn to approximately 4 µm ID at the exit, was utilized as a pressure (flow) restrictor to maintain the pressure in the transfer line to the point of injection.

The Extranuclear single quadrupole mass spectrometer, equipped with a high-flow-rate (HFR) interface and a CI ion source (Figure 1), and interfaced to a supercritical fluid chromatographic oven. The instrument was operated in the CI mode for all studies, using isobutane, ammonia, or the 2-propanol modifier from the mobile phase as the CI reagent. Ion source pressure (including reagent gas, if required) was maintained at approximately 1 torr. The ion source temperature was maintained between 160°C and 220°C. The mass spectrometer was controlled by a Teknivent (Teknivent Corp., St Louis, Missouri) mass spectrometer data system. The supercritical mobile phase was supplied to the chromatographic column using the microprocessor-controlled syringe pump described in an earlier report (Chess and Smith 1986).

The HFR interface probe (Figure 1), constructed from a 1.27-cm-OD (outside diameter) stainless steel tube, is temperature regulated by means of a flow of air heated in a chromatographic oven. The deactivated, fused silica, polished flow restrictor, attached to the exit end of the microbore column with a zero-dead-volume (ZDV) reducing union (Valco), was never longer than 6 cm. The vacuum seal to the probe body was made with a "half-union" that was silver-soldered to a short length of capillary stainless steel tubing (sheath) such that the end of the sheath extended approximately 0.7 cm beyond

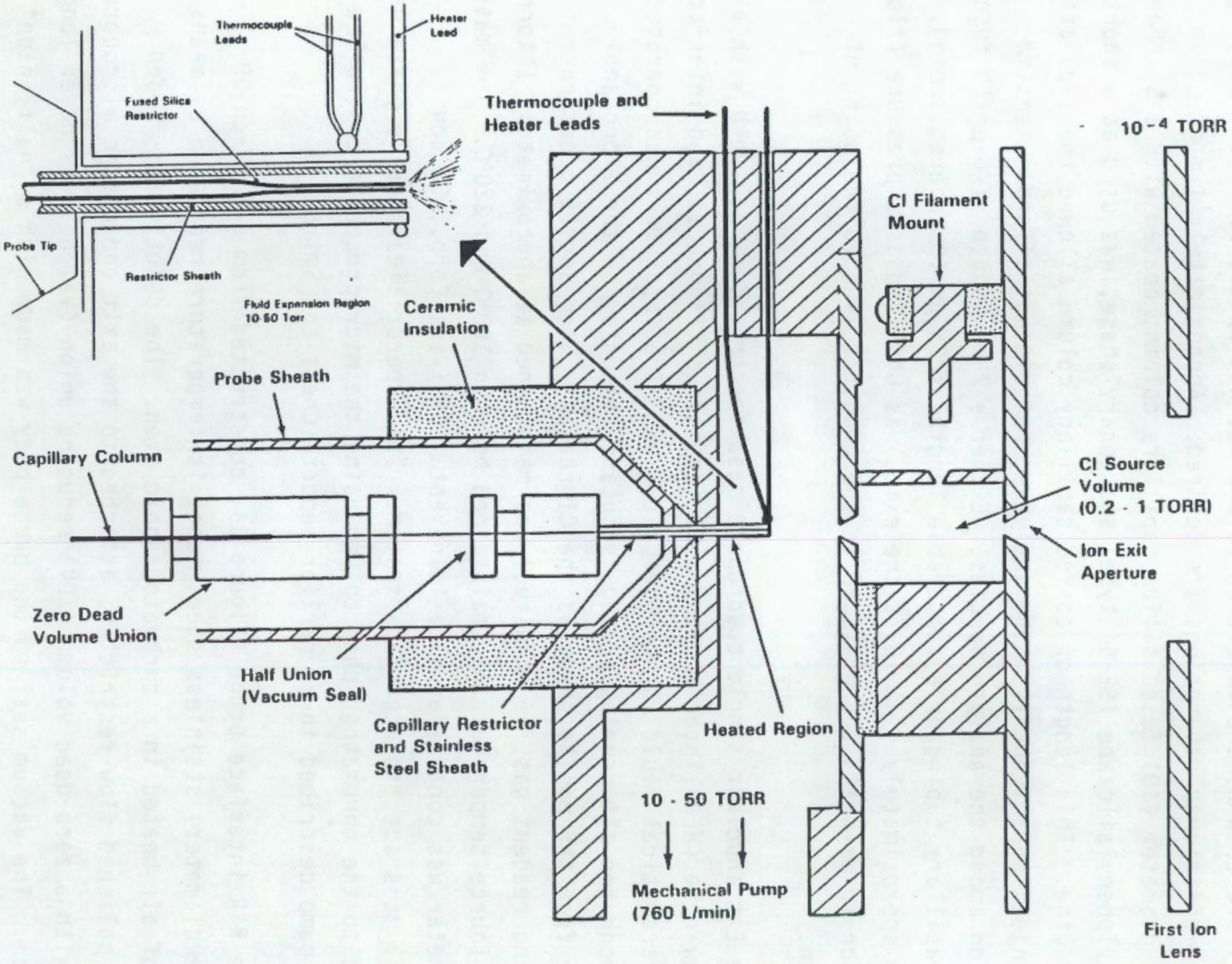

FIGURE 1. Schematic Diagram of the High-Flow-Rate SFC/MS Interface and CI Ion Source Used with a Quadrupole Mass Spectrometer

the end of the probe. This design provided mechanical support of the half-union and strong, mechanical protection for the delicate fused silica restrictor. The capillary sheath (0.5 mm OD) was inserted inside a larger 0.7-mm-ID stainless steel capillary and aligned with an aperture in the CI source repeller electrode. The repeller aperture served as the flow restrictor between the ion source volume and the expansion region, allowing the expansion region to be differentially pumped relative to the ion source volume. The larger-diameter stainless steel capillary tubing was connected to the expansion volume rear wall, a thermocouple, and a high-resistance electrical lead, and served to heat the fused silica restrictor.

Chromatographic separations were performed with a 1.0 mm x 100 mm microbore HPLC column packed with 5-µm silica particles (Alltech Assoc., Deerfield, Illinois) that were coated with a C_{18}-bonded phase (ODS-Hypersil). To minimize dead volumes, the column was placed directly inside the 1.27-cm-OD interface probe (see Figure 2). An HPLC injection valve (Model 7520, Rheodyne Inc., Cotati, California) with a 0.2-µL injection volume was connected to the column with a length of deactivated 50-µm-ID fused silica capillary tubing no longer than 20 cm. Connections to the injector and column were made using ZDV reducing unions (Valco). The temperature of the probe could be controlled to ±1°C along the entire length, and all experiments were conducted with a probe

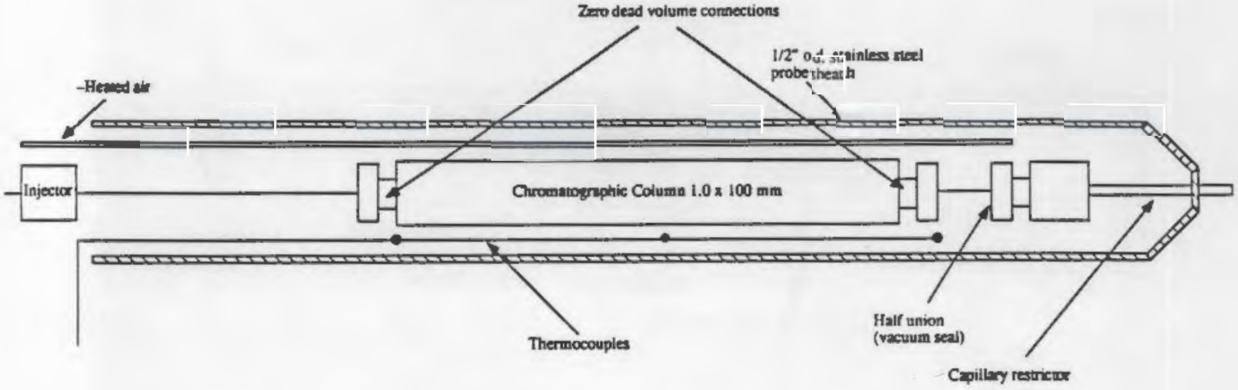

FIGURE 2. Schematic Diagram of the Interface Probe Containing the Microbore HPLC Column Used in the HFR SFC/MS Experiment

temperature of 75°C. A mixture containing 2% (by volume) 2-propanol (Burdick and Jackson, Muskegon, Michigan) in 99.99%-pure anaerobic-grade carbon dioxide (Scott Specialty Gase) was used as the supercritical chromatographic mobile phase.

An Extranuclear triple quadrupole mass spectrometer, equipped with a "simultaneous" dual electron impact ionization (EI)-CI ion source and interfaced to a supercritical fluid chromatograph oven, was operated in the CI mode for SFE and DFI studies. This mass spectrometer was controlled by a Teknivent mass spectrometer data system, which permitted the mass spectrometer to be operated as a conventional quadrupole instrument or as a tandem mass spectrometer. The interface design for this system, detailed in Figure 3, is constructed in a 0.5-in-OD stainless steel tube, which served as the inlet probe for the chromatographic column or transfer line. The probe tip, which housed the pressure restrictor, includes a stainless steel hypodermic tubing heater, similar to the design used for the magnetic sector instrument interface (Chess et al. 1987). Electrical connections for this heater and the associated thermocouple were made inside the probe. The only required modification to the commercial ion source was the enlargement of the entry hole to accept the probe tip and insulating ceramic sleeve.

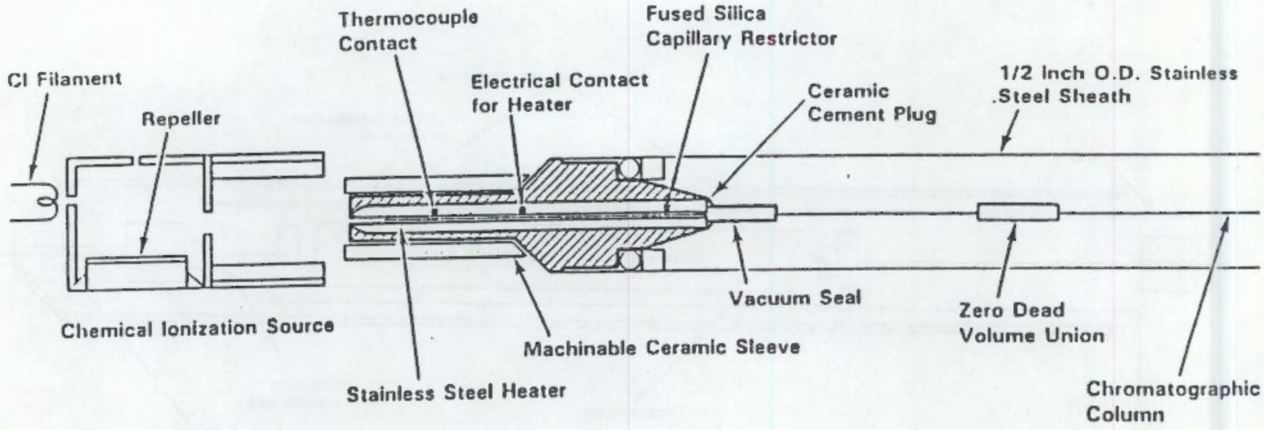

FIGURE 3. Schematic Diagram of the SFC/MS Interface Probe Used with the Triple Ouadrupole SFC/MS Instrument

Total ion source pressure (including reagent gas, if required) was maintained at approximately 2 x 10^{-4} torr. The chromatographic oven, holding the extraction cell or transfer line, was kept at 165°C for studies using methylamine and at 125°C for studies with acetic-acid-modified CO_2. Extraction fluid pressure for these studies was varied under computer control. The stainless steel extraction cell used was a low-dead-volume design capable of holding up to 100 mg of dry sample. Typical sample sizes for the microextractions performed were on the order of several hundred micrograms. The cell was connected to a length (~1 m) of deactivated, 50-µm-ID fused silica capillary tubing that served as a transfer line. Polished restrictors were used to restrict the cell (extraction) pressure. The extraction effluent was continuously monitored with the mass spectrometer as the pressure was increased (from 75 to 400 bar for methylamine; from 150 to 450 bar for acetic acid-modified CO_2). Resulting mass spectra were typically averaged over several scans to provide representative spectra for hard-copy output.

RESULTS AND DISCUSSION

The first technical results topics discussed below cover aspects of enhancing performance of the instrument, such as improving the design and function of the SFC/MS interface region, developing methods for mass calibration, and increasing the overall system safety. Development of polar-modified mobile phases for capillary supercritical fluid chromatography and supercritical fluid extraction is described next, followed by details of the progress made toward the the use of supercritical fluids with the magnetic sector and quadrupole mass spectrometers to analyze complex mixtures derived from fossil fuels.

Improvements to Instrument Performance

The SFC/MS instrument performance was improved in several ways. We redesigned the interface probe's electrical connections to make them more durable. The ion source was modified to allow higher-molecular-weight compounds to be introduced for mass calibration and for evaluation of the interface performance. Further, the manufacture of polished flow (pressure) restrictors for use in SFC/MS and SFE/MS allowed for thicker, sturdier restrictors, which experienced less plugging than flame-drawn restrictors.

Design of the Probe Tip Electrode Contactor and New Safety Features

With the repeated insertion and removal of the DFI probe on the ZAB-2F mass spectrometer, it was found that the copper spring contacts originally designed to make electrical connection to the DFI probe tip (Chess et al. 1987) were not making reproducible contact. The contacts were being bent or pivoted on the support structure, and were not making contact after two or three insertions/removals following adjustment. This misalignment resulted in the inability either to operate the capillary restrictor heater or to read its temperature. The heater has been found to be very important for the transport of higher-molecular-weight materials that have low, but adequate, volatility at higher temperatures and ion source pressures (<1 torr). Without a reliable means of making these contacts, investigations of the ability to transport materials to the ion source were difficult at best, and each readjustment required that the ion source be removed from the mass spectrometer, leading to extensive (expensive) down-time. Eventually, the poor contacts led to heater failure, and the entire probe tip assembly had to be rebuilt.

During the rebuilding period, a new mechanism for making the contacts was designed and manufactured. The contacts are now made with spring-loaded, stainless steel rods mounted in a cylindrical block constructed of Vespel®. Vespel was chosen for this block because it is electrically insulating, has no appreciable vapor pressure or outgassing, and is chemically and physically stable at the operating temperatures of the ion source. A hole in the center of the block accommodates the probe tip. The difference between the outside diameter of the DFI probe and the inside diameter of the Vespel contactor assembly is only 0.010 in., and the rounded ends of the four rods each extend in from the interior surface of the block 0.010 in., allowing for a positive connection even if the probe is slightly off center in the hole. The design ensures that the contact points cannot move from an aligned position when the

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probe is inserted or withdrawn. As the contacts are spring-loaded, there is always a positive force toward the probe tip electrodes to keep the rods in contact. Because the four contact points are symmetrically placed around the ring, the contactor mechanism is self-centering (for the probe shaft) provided that the spring tension on each rod is adjusted equally. The rods are electrically connected to the wire leads via small barrel connectors.

The connector block assembly was attached to the ion source support structure and adjustments made to align the four contacts with the four electrodes of the interface probe tip. Tests of the completed assembly validated the design and construction effort, showing that the probe could be inserted and withdrawn any number of times with no deleterious effects on the alignment of the electrodes. However, the temperature of the probe heater as measured by the thermocouple at any given heating current was lower than for the older design. We do not yet know whether the difference in temperature results from the slightly different placement of the thermocouple on the newly rebuilt heater, or whether it is the reflection of a smaller amount of heating occurring in the heater due to increased resistance of the circuit, which now contains ball bearings and springs. Investigations to determine the cause of the difference in temperatures will be conducted in order to characterize the temperature scale of the probe heater.

Because the probe interface tip is in contact with the ion source of the mass spectrometer, the probe tip electrodes, electrical leads, thermocouple readout, and heater power supply must be maintained at the same electrical potential as the ion source, i.e., 5000 to 6000 V. Therefore, these devices must be electrically isolated from ground potential, and pose a danger to the operator if touched when at high potential. The power supply and isolation transformers have been mounted on the laboratory cart which serves to support the supercritical fluid chromatograph. To offer greater protection to the operator, the sides of the cart have been covered with 0.25-in. thick Plexiglas® plates. Contact with the power supply controls is made via non-conducting standoffs, attached to the power supply control knobs, which

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® Trademark of Rohm & Haas Co., Philadelphia, Pennsylvania extend through the Plexiglas. This arrangement of panels has eliminated the possibility of electrical shock from the high voltage applied to some components mounted on the cart by completely enclosing these components.

Extension of the Mass Calibration Range Under CI Conditions

The current design of the interface between the supercritical fluid chromatograph and the magnetic sector mass spectrometer, developed under this program, has been shown to allow the transport of higher-molecular-weight, less-volatile materials into the ion source than previous designs (Chess et al. 1987). Experimental evaluations of the instrumentation identified two limitations of the system: 1) the inability to mass calibrate the data system to molecular weights higher than approximately 800 amu while operating in the CI mode used for SFC/MS; and 2) the inability to introduce low-volatility, higher-molecular-weight compounds into the ion source in an alternate method to DFI/SFC so as to allow the evaluation of the interface performance. Previous mass calibrations higher than 1000 amu were accomplished in the EI mode using Fomblin oils (Chess and Smith 1986). The problem with this method is that the ion source operating parameters have to be set very differently for EI than for CI, which leads to incorrect mass assignments when a spectrum is acquired in the CI mode using an EI calibration file. The second limitation arises from the lack of a heatable, conventional, direct insertion probe that can be used in a CI experiment.

A proposed single solution overcame both limitations by modifying the ion source design so that the desorption (or direct) chemical ionization (DCI) technique could be employed. The DCI technique provides a means of directly introducing low-volatility compounds directly into the CI plasma within the ion source and desorbing them from the probe tip in a mild, reproducible fashion. Only two modifications were required to implement this technique on the current SFC/MS ion source: 1) to enlarge the entry hole normally used for the solids inlet probe, and 2) to attach the commercially available contacts, which allow electrical connection to the DCI probe, to the ion source.

The ammonia chemical ionization mass spectra of a polyethylene glycol (PEG) sample (AMW 600) obtained using three different modes of sample introduction are shown in Figure 4. Figure 4A is the spectrum of PEG-600 introduced using an unheated solids inlet probe that allows analysis of only the portion of the material that is volatile at the temperature of the probe tip (somewhat less than the 210°C source temperature). This form of sample introduction leads to discrimination against the higher-molecular-weight oligomers of lower volatility and is reflected in the lower relative abundance of these species in this mass spectrum compared to the others in Figure 4. Figure 4B depicts the mass spectrum of the same sample introduced using the DCI probe. In this case the oligomer distribution more accurately reflects the actual amounts of each oligomer present in the sample, as determined by other techniques. This spectrum is very similar to that produced by introducing the sample by direct fluid injection using a supercritical fluid, shown in Figure 4C. The relative abundances of the higher-molecular-weight oligomers are similar in Figures 4B and 4C, but the DFI spectrum (4C) shows a higher abundance of lower-molecular-weight fragment ions (the ions not enumerated with molecular-weight information) and higher abundances of the lower-molecular-weight oligomers. The difference in distribution of lower-molecular-weight oligomers between the DCI and DFI spectra is not currently understood. The greater abundance of fragment ions in the DFI spectrum is believed to be caused by partial thermolysis (pyrolysis) of the sample in the heated restrictor region of the DFI probe. For the example shown in Figure 4C the heater temperature was 390°C. The actual temperatures of the fluid and sample are not directly measured, but would be lower than 390°C due to the poor thermal conductivity of the fused silica restrictor and to the cooling of fluid and restrictor during the supercritical fluid expansion process.

The DCI process, however, is still limited by restricted application because of sample volatility (or lack thereof) and sample thermal lability. For example, the mass spectra resulting from the analysis of PEG of AMW 1000 (PEG-1000) by the three previously compared techniques are given in Figure 5. The mass spectrum from the analysis using the unheated probe (Figure 5A) indicates the limit, due to volatility at the probe/source temperature used

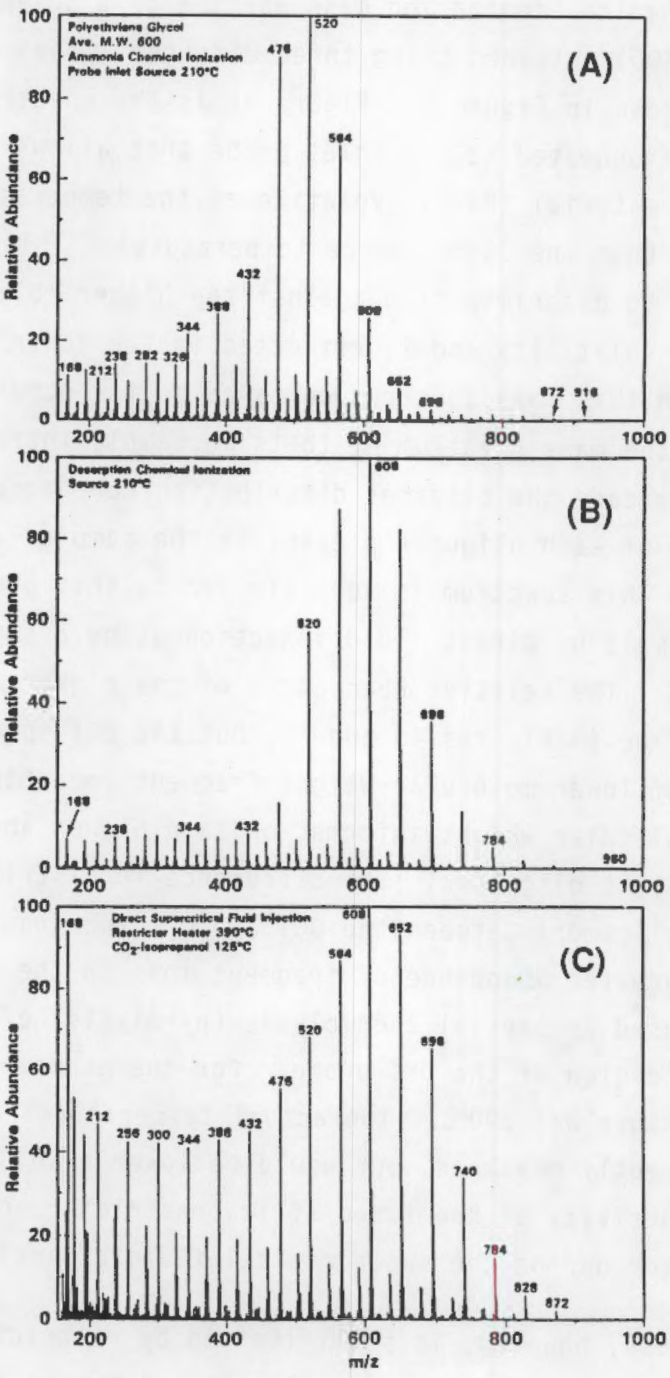

FIGURE 4. Ammonia Chemical Ionization Mass Spectra of Polyethylene Glycol, Average Molecular Weight 600, Admitted to the Ion Source by A) Unheated Direct Probe, B) Desorption Chemical Ionization Probe, and C) Direct Supercritical Fluid Injection.

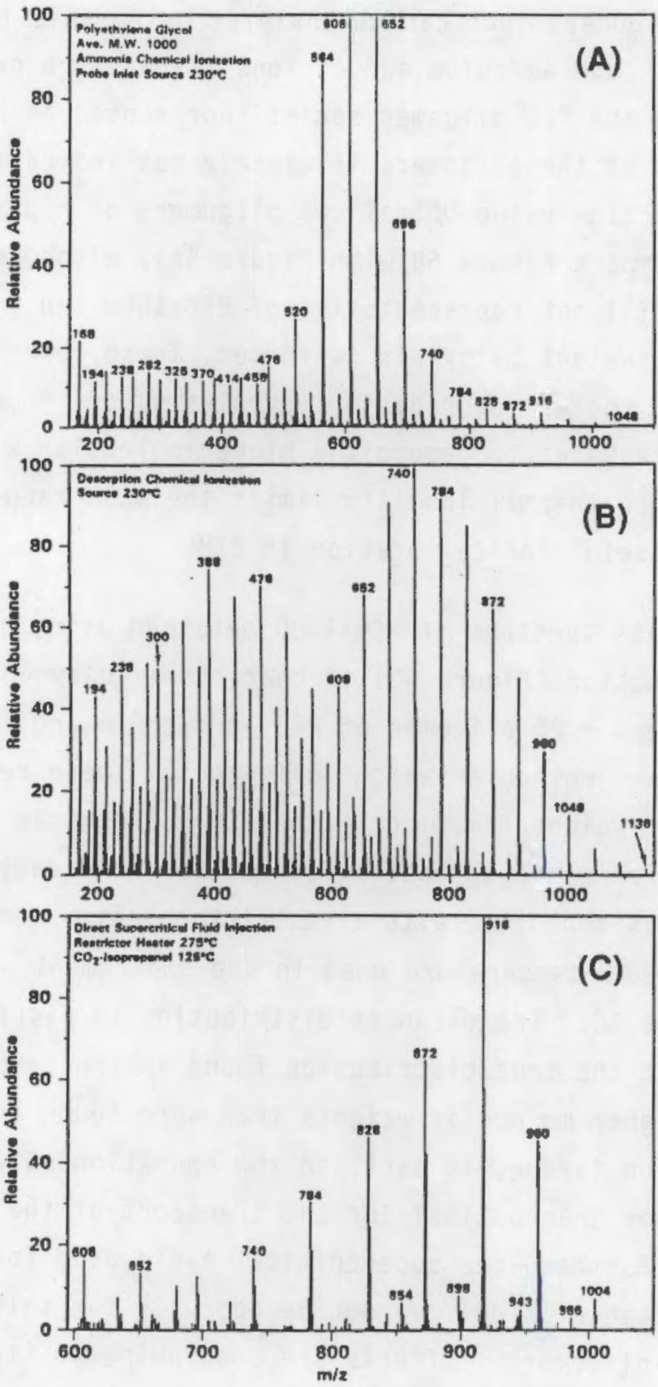

FIGURE 5. Ammonia Chemical Ionization Mass Spectra of Polyethylene Glycol, Average Molecular Weight 1000, Admitted to the Ion Source by A) Unheated Direct Probe, B) Desorption Chemical Ionization Probe, and C) Direct Supercritical Fluid Injection.

(230°C), of PEG oligomers that can be analyzed using this type of sample introduction. Although ammonium adduct ions ($M+NH_4$) are present for oligomers up to n = 23 (with the PEG oligomer series represented as $H(CH_2CH_2O)_nH$), the relative abundance of the oligomers is clearly not indicative of a sample of PEG-1000. Introduction using DCI allows oligomers of higher molecular weight to be analyzed (compare Figure 5B with Figure 5A), although the oligomer distribution is still not representative of PEG-1000 and a significant amount of lower-molecular-weight materials is formed. These lower-molecular-weight species arise from thermal degradation (pyrolysis) of the PEG-1000 sample at the temperatures required to desorb the higher-molecular-weight oligomers from the DCI probe. Such thermal lability limits the mass range over which PEG mixtures will be useful for calibration in CIMS.

The NH_3-CI mass spectrum of PEG-1000 obtained using supercritical DFI for sample introduction (Figure 5C) is characterized by an abundant ammonium adduct ion for the n = 20 oligomer of PEG at m/z 916 and low relative abundances for lower-molecular-weight oligomers. These results indicate that a higher-molecular-weight fraction of the PEG-1000 sample is being introduced to the CI ion source without substantial thermal degradation of the sample. This experiment was conducted with a restrictor heater temperature of 275°C, compared to the 390°C temperature used in the experiment used to produce the spectrum in Figure 5C. The oligomer distribution in Figure 5C does not accurately reflect the true distribution found in the sample, which contains oligomers with higher molecular weights than were found in the DFI results. This discrimination is due, in part, to the operation of the DFI interface at a temperature lower than optimal for the transport of the higher-molecular-weight species. Further, the supercritical fluid used for this sample (5% v/v 2-propanol in carbon dioxide) may not be adequate for solvating the higher-molecular-weight oligomers. Efforts are continuing to improve the performance of the DFI/SFC-MS system for the analysis of the higher-molecular-weight, lower-volatility samples.

The NH_3-CI spectra of mixtures of PEG oligomers in Figures 4 and 5 show characteristics useful for a mass calibration standard: a series of intense, regularly spaced masses, extending over a broad mass range, with readily calculated exact masses. However, the results from the experiments discussed above indicate that the upper mass limit for using PEG oligomers as mass calibration standards appears to be approximately 1200 daltons when using mixtures of PEG-600 and PEG-1000. Binary mixtures of PEG-1000 and PEG-1500 have been used to calibrate to 1400 daltons using ammonia as the CI reagent gas. When efforts to desorb higher-molecular-weight oligomers of PEG were made by increasing the current on the DCI wire, the sample yielded a larger percentage of lower-molecular-weight species, without desorbing intact higher-molecular-weight oligomers.

2-Propanol was also investigated as a CI reagent gas for calibration during operation in the on-line SFE/MS mode. 2-Propanol was found to be a mild CI reagent, yielding predominantly protonated molecular ions for the oligomers of PEG found in the binary mixture of PEG-1000 and PEG-1500 samples. The magnetic sector DFI/MS instrument was calibrated to appoximately 1100 daltons using the 2-propanol reagent gas and DCI introduction of the PEG mixture. The computer calibration files used for this experiment did not contain adequate information to allow calibration to masses higher than 1100 daltons, but there was evidence from the mass spectra that calibration to at least 1400 daltons should be feasible once the calibration files are properly modified.

Remaining to be evaluated are other higher-molecular-weight polymer mixtures as mass calibrants in the CI mode. There are literature reports that mixtures of polydimethylsiloxanes have been used to calibrate to about 800 daltons under high-resolution conditions, and mixtures containing higher-molecular-weight oligomers may allow calibration to higher values. Polydimethylsiloxane mixtures of AMW 770 and 3900 (Polysciences, Inc., Warrington, Pennsylvania) have been acquired for testing. We also plan to examine poly(ethylenimine) mixtures of AMW 600 and 1200 (Polysciences) as potential mass calibration standards.

Use of Polished Restrictors for SFC/MS and SFE/MS

The inadequacy of straight, fused silica capillaries for use as pressure restrictors in SFC/MS and SFE/MS prompts the continued search for other types of restriction. The necessary-but-undesirable use of metal restrictors for highly solvating fluids such as methylamine and ammonia indicates the need to remove ZDV unions (and the required polymer ferrules) from supercritical fluid systems. Although drawn capillary restrictors do offer some advantages, such as better thermal conductivity through thinner walls (to aid in transport of less volatile materials) and the possibility of integration by flame-drawing the restrictor directly on the end of the column or transfer line, they are far from ideal. The drawn restrictors have a long, uncoated length of fused silica that is extremely fragile, making them difficult to handle. They are best made from capillary tubing having a small outside diameter, making them difficult to seal in unions and vacuum seals. Finally, they can generally be used only once; if they plug or break, a new restrictor needs to be fabricated from new material because repairs cannot be made.

An alternative design has been reported for use with flame ionization detectors (Guthrie and Schwartz 1986) in which the end of a capillary tube is sealed in a flame and then polished open by careful abrasion with emory cloth or 600 grit sandpaper. Manual preparation of this type of restrictor is tedious: the best fabricators take 30 minutes to produce one restrictor. We have developed a means of producing this type of restrictor in less than 5 minutes. However, restrictors are still being fabricated independently of the column or transfer line. Therefore, ZDV unions are still required to attach the polished restrictors to the ends of the columns or transfer lines. When it is clear that these polished restrictors are a viable means of flow restriction for SFC, the restrictor could be fabricated directly on SFC capillary columns and SFE transfer lines, thus creating "integral polished restrictors" and minimizing "dead volume."

The manufacture of these polished restrictors enables the use of capillary tubing of approximately 370 µm OD (approximately 50 µm ID). This larger OD strengthens the restrictors, which are less likely than the thinner variety to break on insertion and assembly, and which can be held more readily in unions and vacuum seals. Still to be determined, however, is whether the heavier-walled tubing might limit the transfer of less-volatile analytes because the thicker fused silica is a poorer thermal conductor than the thinner-walled tubing. Results from preliminary studies have not shown any variation in performance compared with those from experiments conducted with straight or drawn capillaries, but a rigorous test has not yet been conducted. Samples that have been analyzed with the polished restrictors include coal/petroleum co-processing samples and fuel sediments, and these restrictors have been used on both the magnetic sector and quadrupole instruments.

Characterization of Polar and Polar-Modified Mobile Phases

The study of pure and mixed supercritical solvents for use with higher-molecular-weight materials involved a variety of experimental procedures. Ammonia, methylamine, and carbon dioxide modified with acetic acid were examined by means of SFE/MS, and the phase behavior of the latter fluid was examined optically.

Use of Ammonia and Methylamine as Supercritical Solvents

The use of more-polar supercritical fluids (more polar than relatively nonpolar fluids such as CO_2, methane, and ethane) for the analysis of more-polar and higher-molecular-weight fuel materials is being actively pursued in this research program. Ammonia (NH_3, $T_c = 133°C$, $P_c = 113$ bar) has been found to solvate higher-molecular-weight materials than were soluble in either pure hydrocarbon fluids (pentane or smaller alkanes) or alcohol-modified hydrocarbon fluids (e.g., pentane-ethanol). However, the use of ammonia is limited by its high reactivity with the polymeric materials used in ferrules for unions and as coatings on fused silica capillary columns. In an effort to avoid the reactivity of supercritical ammonia while maintaining a polar, highly solvating fluid, methylamine (CH_3NH_2) was chosen as a substitute. The critical temperature of methylamine is only slightly higher than that of ammonia ($T_c = 157°C$); the critical pressure ($P_c = 75$ bar) is lower.

Currently, the only means of providing a DFI transfer line without using polymeric ferrules in the mass spectrometer systems is by using a transfer line made entirely from platinum-iridium (Pt-Ir) tubing (100-µm ID) that can be pinched on the end to cause a restriction in the flow and thereby maintain pressure in the transfer line. The current design of the interface to the magnetic sector DFI/MS instrument does not permit the use of a metal transfer line and/or a metal restrictor because the metal tubing would act as a path to ground for the high electrical potential found in the ion source during normal operation. The interface to the triple quadrupole DFI/MS system does not have this limitation because the ion source does not operate at high voltage. Therefore, this instrument was used to determine the practicality of using methylamine as a supercritical solvent for DFI/MS.

The sample chosen for analysis using methylamine was a sediment formed in marine diesel fuels. The sediment was known to contain atom-percents of nitrogen and oxygen higher than those found in the fuels from which it was isolated, and had proven difficult or impossible to characterize using other analytical techniques, usually because of insolubility and involatility. Figure 6 depicts representative methane CI mass spectra of this sediment obtained during SFE/MS analysis using methylamine as the extracting fluid. The mass spectra indicate sediment components with molecular weights in excess of 600 daltons. Because the presence of methylamine in the ion source did not appear to affect the acquisition of methane and ammonia CI mass spectra of standards injected by means of a methylamine fluid under the same conditions used for the DFI/MS analyses, the mass spectra in Figure 6 are assumed to accurately represent methane CI spectra. These experiments indicate that methylamine may prove to be a useful supercritical solvent for higher-molecular-weight, fuel-related materials as long as the instrumentation used prevents contact of the fluid with polymeric materials.

Use of Acetic Acid-Modified Carbon Dioxide as a Supercritical Solvent

In conjunction with the use of the basic supercritical polar fluids ammonia and methylamine, there is a need for acidic supercritical fluids. Our experience with sulfur dioxide has shown that its solvating powers were

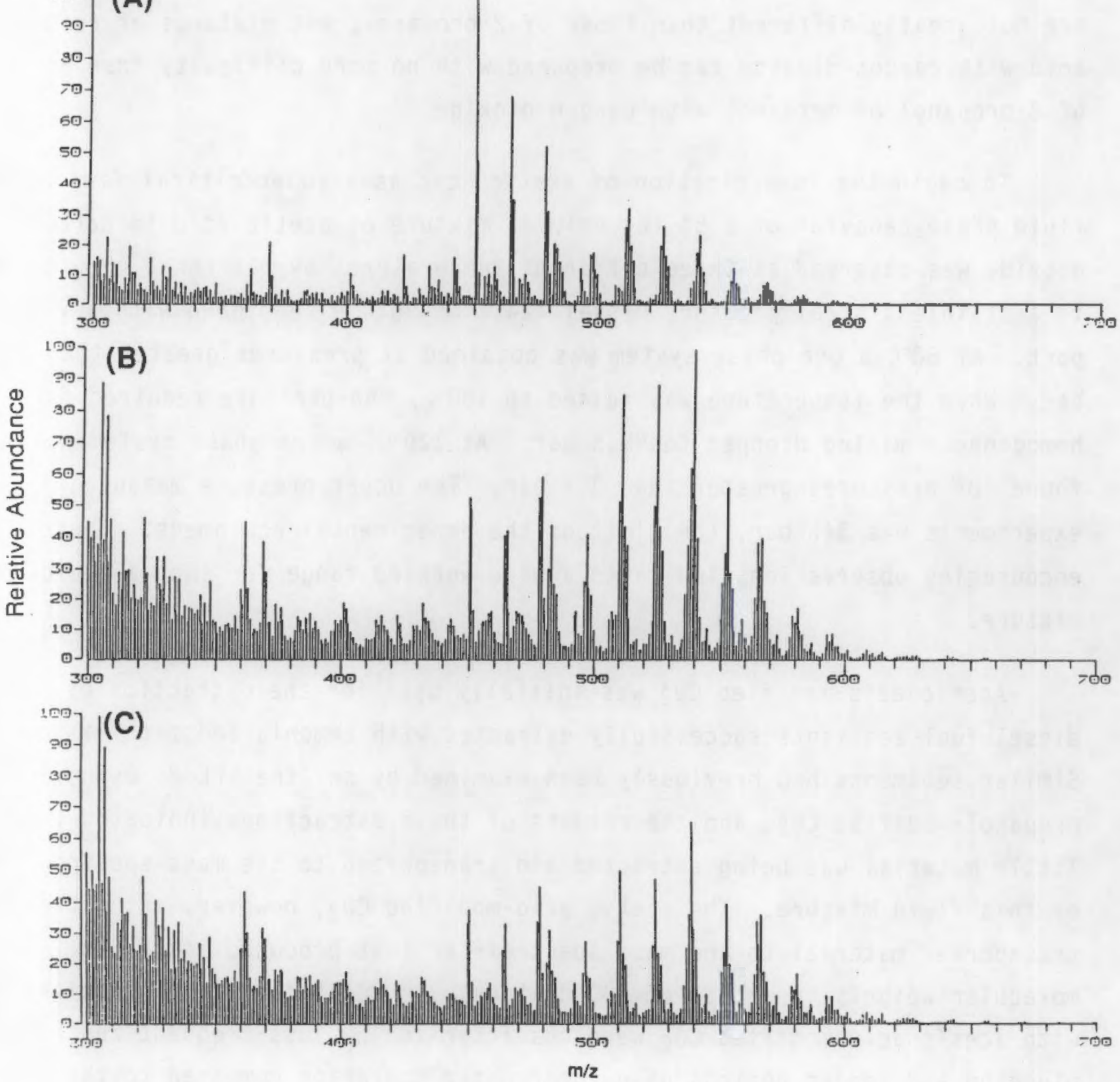

FIGURE 6. Methane CI Mass Spectra of a Marine Diesel Fuel Sediment Acquired by SFE/MS Analysis Using Methylamine at 165°C and with Fluid Pressures of (A) 300 bar, (B) 350 bar, and (C) 400 bar

similar to easier to handle fluids, such as carbon dioxide and nitrous oxide. The added problems of corrosion and irritation associated with this fluid caused continued search for other fluids. The next fluid examined was acetic acid. The critical conditions for acetic acid (T_C = 594.4 K; P_C = 57.1 bar) are not greatly different than those of 2-propanol, and mixtures of acetic acid with carbon dioxide can be prepared with no more difficulty than mixtures of 2-propanol or methanol with carbon dioxide.

To begin the investigation of acetic acid as a supercritical fluid, the fluid phase behavior of a 5% (by volume) mixture of acetic acid in carbon dioxide was observed at three different temperatures over a range of pressures in a stainless steel pressure vessel (24.2-mL volume) equipped with a view port. At 80°C a one-phase system was obtained at pressures greater than 115 bar. When the temperature was raised to 100°C, the pressure required for homogeneous mixing dropped to 98.5 bar. At 120°C, a one-phase system was found for pressures greater than 3.4 bar. The upper pressure measured in all experiments was 345 bar, the limit of the experimental equipment. These encouraging observations indicated a wide working range for such a fluid mixture.

Acetic acid-modified CO_2 was initially used for the extraction of the diesel fuel sediments successfully extracted with ammonia and methylamine. Similar sediments had previously been examined by on-line SFE/MS using 2-propanol-modified CO_2, and the results of these extractions indicated that little material was being extracted and transported to the mass spectrometer by this fluid mixture. The acetic-acid-modified CO_2, however, extracted and trasnported material to the mass spectrometer that produced ions with molecular weights in excess of 600 daltons. In addition, the extractions made with acetic acid-modified CO_2 were characterized by less-frequent restrictor plugging and longer periods of uninterrupted operation compared to the extractions made with 2-propanol-modified CO_2.

Figure 7 is an averaged CI mass spectrum of the acetic acid-modified CO_2 (5.6% acetic acid, by volume) extract of a diesel fuel sediment acquired at an extracting pressure of 350 bar. The masses at m/z 163-165 and m/z 181-183

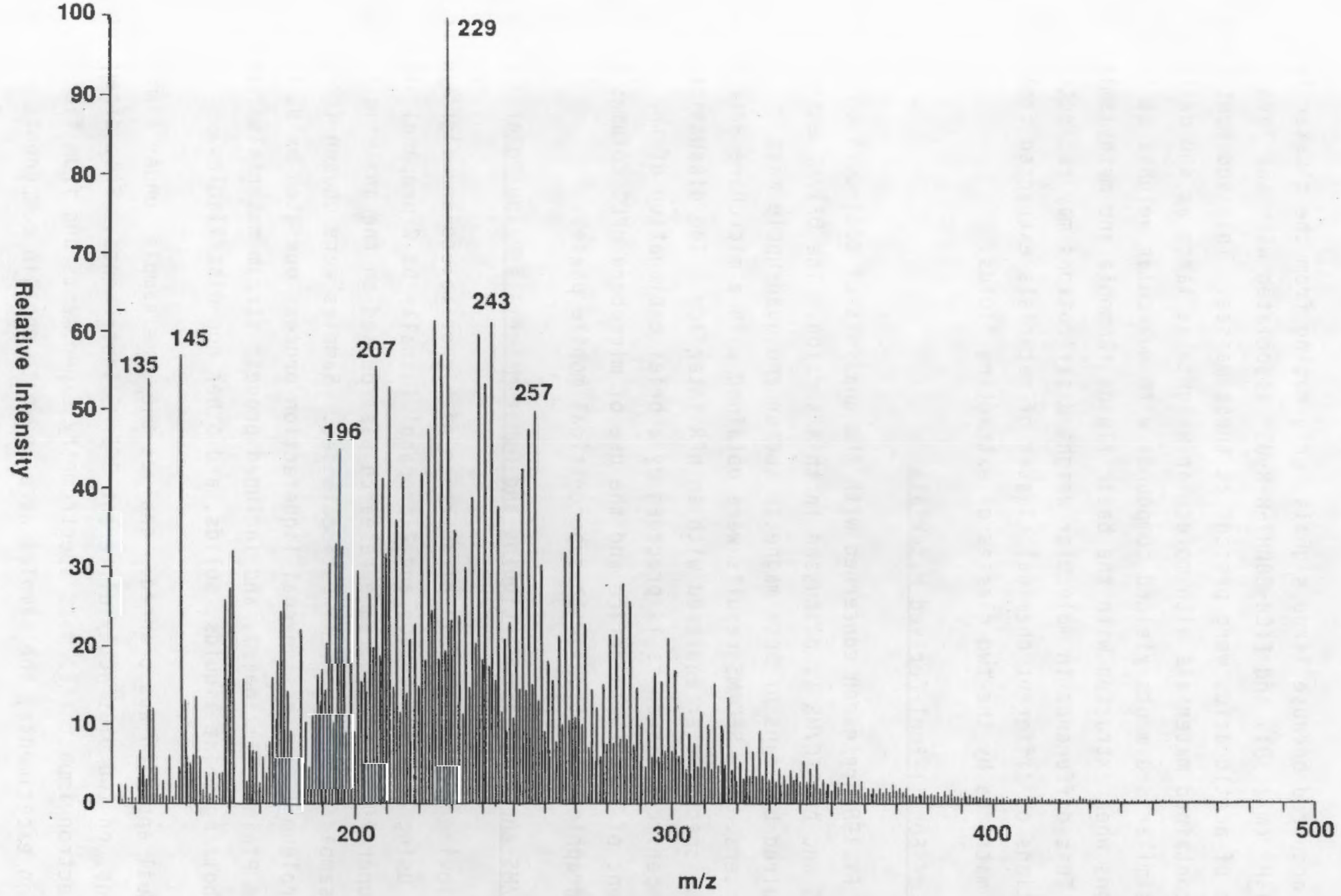

FIGURE 7. CI Mass Spectra of a Marine Diesel Fuel Sediment Acquired by SFE/MS Analysis Using a 5.6% (v/v) Acetic Acid/CO_2 Fluid at 148°C and with Fluid Pressure of 350 bar

were not acquired because large signals, originating from the cluster ions $(CH_3COOH)_3H^+$ (m/z 181) and $[(CH_3COOH)_3H-H_2O]^+$ associated with the large abundance of acetic acid, were present at these masses. This sediment sample extract contained materials with molecular weights as large as 400 daltons, whereas similar sediments yielded compounds with molecular weights as large as 600 daltons when extracted with the basic fluids (ammonia and methylamine, see above). This difference in molecular weight distributions may reflect the distributions of different chemical classes of materials extracted from the sediment matrices by the two classes of extracting fluids.

Analysis of Fossil-Fuel-Derived Materials

The FY 1987 research concerned with the analysis of coal-derived liquids by DFI/MS and by SFC/MS is discussed in this section. The DFI/MS experiments were acquired by means of both magnetic sector and quadrupole mass spectrometers. The SFC/MS results were obtained with a microbore HPLC column and a mass spectrometer equipped with an HFR interface. The discussion of the SFC/MS experimental results is preceded by a brief explanation of the development of the HFR interface and the use of microbore HPLC columns for chromatographic separations with supercritical mobile phases.

DFI/MS Analysis of Coal Liquids and Other Materials Using Polar Fluids

Following the successful introduction of higher-molecular-weight polar polymers using mixtures of CO_2 and 2-propanol (usually 5% 2-propanol in CO_2) as the supercritical fluid, some research has focused on the analysis of fuel-related samples using the same methodologies. Samples were chosen from a coal/petroleum co-processing coal liquefaction process operated by U. O. P., Inc. (Des Plaines, Illinois), and included process stream materials composed of high-boiling-point liquids, solids, and other non-distillables.

A dual approach was planned: analyze the same sample, under similar conditions, on two distinctly different DFI/MS instruments. From direct probe 12-eV electron impact (EI) mass spectrometry experiments and from field desorption experiments, the samples were known to contain components with molecular weights in excess of the mass range of the triple-quadrupole DFI/MS instrument (about 1000 daltons), and above the mass range of the current limit of calibration in the CI mode on the magnetic sector DFI/MS instrument (about 1400 daltons). By using the same fluid composition, sample size, transfer line material and restrictor design, we planned to compare the operation of the different DFI interfaces on the two instruments to determine whether the higher-molecular-weight materials were being transported more efficiently through one interface than the other. If both interfaces appeared to transfer material equally at lower masses, the results would indicate the extent to which the quadrupole system was discriminating against higher-molecular-weight ions. This important information would be convoluted to some extent with the differences in the ionization efficiencies of the two ion sources and with any inherent differences in operation of the two restrictors.

Experiments were first conducted using straight lengths of 6-µm-ID fused silica capillary as the pressure (flow) restrictor. This tubing had been found in other studies to give flow rates adequate for reproducible SFC/MS analysis on both instruments. We injected a sample size of 60 nL (without splitting the sample) onto a 1-m length of deactivated fused silica tubing (50 µm ID) used as a transfer line. Unfortunately, the experimental results from both instruments presented difficulties and could not be interpreted to yield information about interface or intrument performance. For the quadrupole system, ions related to the sample were detected at the same time as those originating from the solvent (due to the poor efficiency of the column used for the separations). The presence of the intense solvent signals made the sample data non-reproducible and difficult to interpret. During experiments with the magnetic sector instrument, the capillary flow restrictor plugged during the elution of the sample, apparently because the sample was still largely dissolved in the injection solvent, and had not entered the supercritical fluid mobile phase before expanding. Upon decompression in the flow restrictor, the solvent volatilized, leaving the non-solvated sample to plug the restrictor.

The problems could not be overcome by adjusting restrictor temperature or position in the heated zone, by removing the polyimide coating to aid in the heat transfer, or by slightly changing the flow rate by altering restrictor length. The use of a sample splitter, positioned immediately after the injector valve on the magnetic sector instrument, was investigated as a means of removing the bulk of the solvent to allow more efficient sample partition into the supercritical fluid phase. The splitter was ineffective, however; its use resulted in either plugged restrictors or the production of spectra containing no signals from the sample because, after the sample split, the amount of sample entering the ion source was extremely small. A larger fused silica restrictor (12 µm ID) was also investigated as a potential solution to the plugging problem. The decreased restriction led to higher flow rates, which greatly reduced the frequency of plugging, but which also raised the ion source pressure so high with this instrument that auxiliary CI reagent gases, such as methane, isobutane, or ammonia, could not be used. Therefore, the mobile phase, a mixture of up to 5% 2-propanol in CO_2, had to be used as the CI reagent gas. Future experiments with the high flow rate interface should successfully resolve these problems.

Results from DFI/MS analyses, performed with both instruments, of single compounds representing a wide variety of chemical functional groups indicated that 2-propanol is a mild CI reagent gas, yielding principally protonated molecular ions for most analytes of interest (slightly to moderately polar compounds of moderate molecular weights of 200-500 daltons). However, major differences were found in some of the spectra of the same components acquired on the two instruments. For example, Figure 8 shows the 2-propanol/CO_2-CI mass spectra of one model compound, Famphur (an organophosphorous pesticide of nominal molecular weight 325 daltons), acquired on the triple quadrupole DFI/MS system (A) and on the VG ZAB-2F magnetic sector instrument (B). In both spectra the base peak is the protonated molecular ion, m/z 326, indicating the transport of the intact molecule into the ion source, even though this compound has a low volatility and is thermally labile. However, the spectrum obtained on the magnetic sector instrument (Figure 8B) shows significant fragment ions at m/z 218 and m/z 202, which correspond to

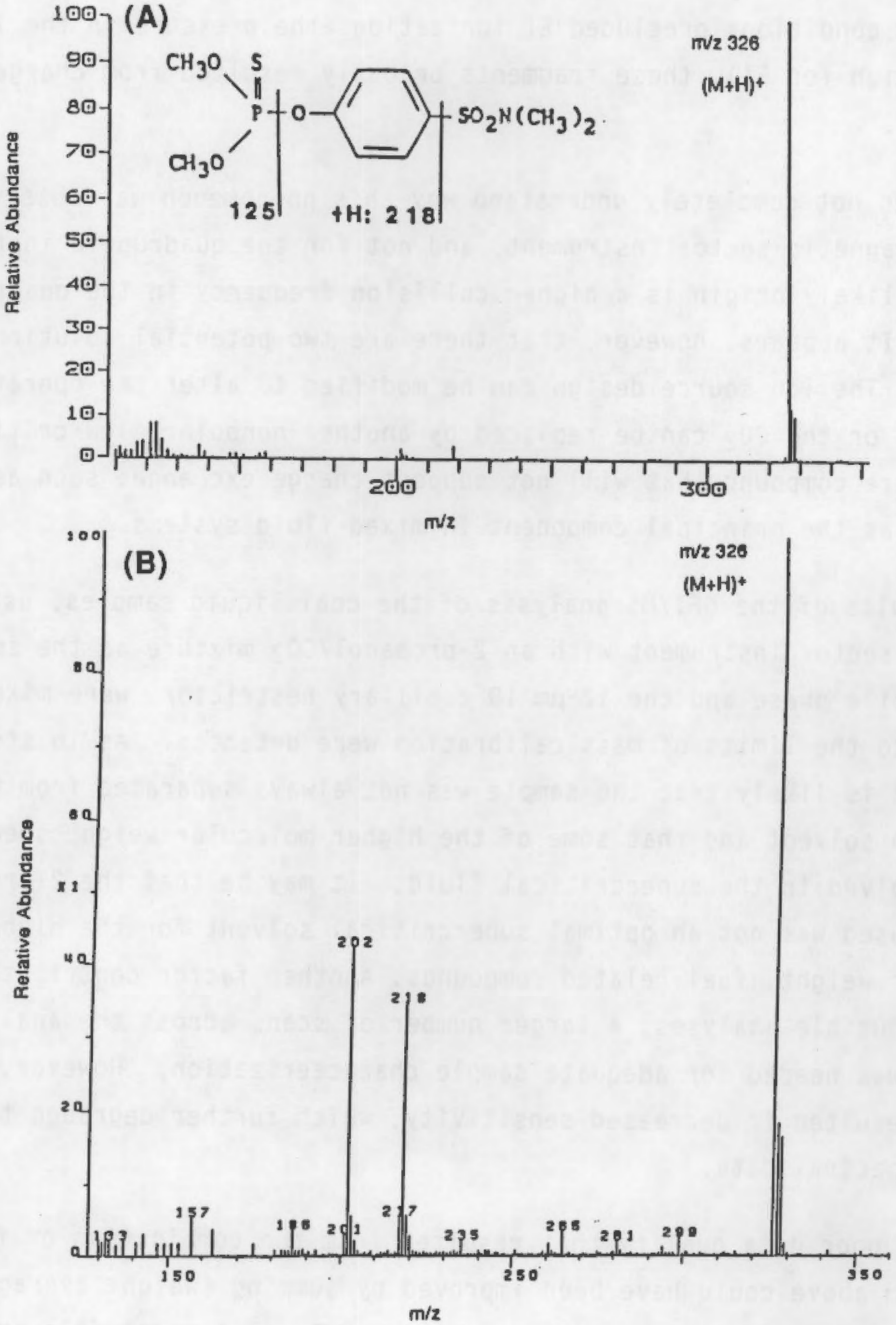

FIGURE 8. IPA CI Mass Spectra of Famphur Obtained from DFI/MS Analysis Using (A) the Triple Quadrupole Instrument and (B) the Magnetic Sector Instrument

fragments found for EI ionization conditions. Because the ion source operating conditions precluded EI ionization (the pressure in the ion source was too high for EI), these fragments probably resulted from charge exchange with CO_2^+.

We do not completely understand why this phenomenon was observed only for the magnetic sector instrument, and not for the quadrupole instrument, but the most likely origin is a higher collision frequency in the quadrupole ion source. It appears, however, that there are two potential solution to this problem. The ion source design can be modified to alter the operating pressure, or the CO_2 can be replaced by another nonpolar, low-critical-temperature compound that will not support charge exchange, such as ethane or propane, as the principal component in mixed-fluid systems.

Results of the DFI/MS analysis of the coal liquid samples, using the magnetic sector instrument with an 2-propanol/CO_2 mixture as the supercritical fluid mobile phase and the 12-µm ID capillary restrictor, were mixed, although ions up to the limits of mass calibration were detected. As in studies noted above, it is likely that the sample was not always separated from the injection solvent and that some of the higher-molecular-weight species were not dissolved in the supercritical fluid. It may be that the 2-propanol/CO_2 mixture used was not an optimal supercritical solvent for the higher-molecular-weight, fuel-related compounds. Another factor contributed to nonreproducible analyses; a larger number of scans across the analyte elution profile was needed for adequate sample characterization. However, faster scan speeds resulted in decreased sensitivity, which further degraded the quality of the spectral data.

The poor data quality that resulted from the combination of factors discussed above could have been improved by summing (weight averaging) the spectral data acquired across the entire sample elution profile and representing the data in one composite mass spectrum. This spectral averaging was not possible, however, with the existing version of data system software, which contains a serious "bug" in the spectral averaging programs. The software manufacturer has been contacted many times during the past 18 months regarding a solution to this problem. It should be noted, however, that these problems are not fundamental in nature, but simply reflect shortcomings of our current data system software. When the software problems have been solved, the comparative studies can be completed.

The HFR Interface and SFC with Microbore HPLC Columns

Even though the highest-resolution SFC is afforded by employing capillary columns, the analysis of complex mixtures of high-molecular-weight, relatively nonvolatile analytes by capillary column SFC is limited by a number of factors. Currently, nearly all capillary SFC employs split-injection techniques in which only a small portion of the sample is introduced to the chromatographic column and detector. Split-injection techniques are not greatly reproducible and are constrained by small sample sizes because of the sample volume, the limited solubility of analytes in the sample solvents, and the potential for overloading thin-film capillary columns. The use of capillary flow restrictors in SFC is, in turn, limited by solute precipitation of nonvolatile analytes, particularly at the low flow rates typically encountered with capillary SFC. These limitations are not present for SFC conducted with conventional and packed microbore HPLC columns, which explains our interest in investigating the latter techniques.

The HFR interface was developed to allow operation at high fluid flow rates, permitting the use of microbore HPLC columns for SFC and enhancing sensitivity for relatively nonvolatile compounds (Smith and Udseth 1987). Similar to other capillary interfaces, the HFR SFC/MS interface probe (Figure 1) is constructed from stainless steel tubing and is temperature regulated using a flow of air heated in a chromatographic oven. The key feature of the interface is an expansion region behind the CI volume into which the supercritical column effluent expands. This region is pumped directly through a 1.2-cm-ID port by a two-stage mechanical pump. The CI reagent gases (methane, isobutane, ammonia, etc.) can be introduced to the CI volume by an additional inlet line (not shown in Figure 1). The design contains provisions for heating the capillary flow restrictor, which aids in the transport of less-volatile analytes to the CI source volume. Compared with other capillary direct-injection interfaces, the HFR interface has the advantages of 1) allowing SFC operation at high flow rates, 2) providing efficient analyte transfer to the CI region, 3) allowing unrestricted CI operation at optimum pressure, and 4) maintaining normal CI reagent gas flow rates while requiring only a relatively minor increase in complexity. The design does not, however, permit operation of ion sources that operate at high voltages, such as magnetic sector instruments (Chess and Smith 1986), which limits its utility to quadrupole instruments at this time. The quadrupole mass spectrometer with this interface has a nominal 1500-dalton mass range, however, which permits analysis of higher-molecular-weight compounds.

The ability to operate at high fluid flow rates permits the use of packed microbore HPLC columns for SFC/MS. The disadvantages of packed columns (compared with capillary columns) include the lower chromatographic resolution and the greater retention of higher-molecular-weight and highly polar analytes. The advantages of this type of column accrue from its higher effective phase ratio compared with 50-µm-ID fused silica capillary columns (greater amount of stationary phase per unit area), resulting in a greatly increased sample size. The larger sample can be injected on-column as a splitless injection, which enhances sensitivity and dynamic range for a given sample concentration. A large effective dynamic range is essential for the complete analysis of extremely complex mixtures associated with fuels and coal-derived liquids. The selectivity of a separation can be enhanced by the wide range of commercially available stationary phases found in HPLC columns.

One method to improve the chromatography of the more highly retained components in packed-column SFC is to add small amounts (1 or 2%) of a polar modifier to supercritical carbon dioxide. This low concentration of modifier, usually methanol or 2-propanol, is not sufficient to increase significantly the solvating power of the fluid for more polar analytes, but is sufficient to interact with, and effectively eliminate, many active sites on the surface of the HPLC stationary phase. A drawback of this approach is that early eluting components are often retained even less in the presence of the modifier, and the chromatographic resolution among these materials is decreased.

The application of pressure programming with packed-column SFC and a polar-modified fluid (a technique widely practiced with capillary columns) would allow full utilization of the selectivity of the chromatographic stationary phase and the variable solvating power of the fluid, a key advantage of supercritical fluids. Short (100-mm) microbore (1- or 2-mm-ID) packed columns would be required to limit the pressure drop across the column because SFC requires uniform pressures to maintain uniform solvating powers. All extra column volumes (or dead volumes) would need to be minimized to eliminate contributions of extra column band broadening and the loss of separation efficiency. A mass spectrometer would be an ideal detector, as it is virtually unaffected by the polar modifier and is selective and sensitive for detecting a wide variety of samples. Furthermore, mass spectrometry would add an extra dimension of selectivity with the ability to identify components not fully resolved chromatographically on the short packed columns.

Microbore SFC/MS Analysis of Coal Liquids

The nitrogen-containing polycyclic aromatic hydrocarbon (NPAC) chemical class fractions (Later et al. 1981) of 700-750°F and 750-800°F boiling point cuts of an SRC-II (Solvent Refined Coal-II) heavy distillate product were analyzed using microbore SFC/MS. The NPAC chemical class fraction is composed primarily of nitrogen-containing polycyclic aromatic hydrocarbons, in which the nitrogen is present as primary, secondary, and tertiary amines, including the indole- and carbazole-NH and aza-N moieties. The mass spectra shown in Figures 9A and 9B are the summations (averages) of all the mass spectra acquired during the SFC/MS analyses of these two boiling-point fractions, and represent an integrated view of all the material entering the mass spectrometer ion source from the column that was ionized under the conditions of the experiment. The chemical ionization conditions were such that protonated molecular species were formed with a minimum of fragmentation. The compounds in the spectrum in Figure 9A (700-750°F fraction) with protonated molecular ions at m/z 182, 196, 210, 224, 238, 252, etc., can best be represented as members of the homologous series of alkylated carbazoles. The base peak (i.e., the most abundant peak) at m/z 196 is attributed primarily to

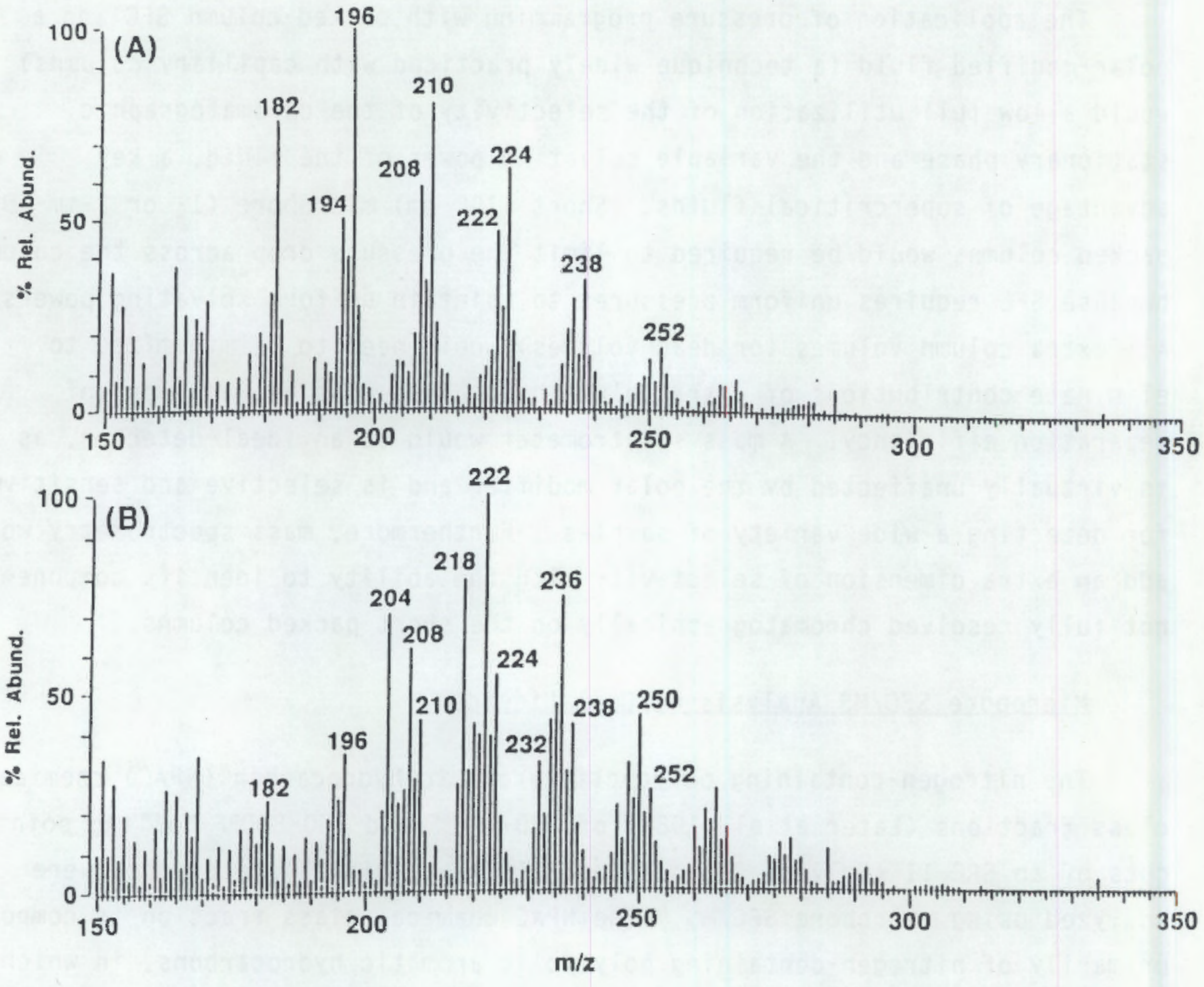

FIGURE 9. Scan-Averaged Mass Spectra from the Microbore SFC/MS Analysis of NPAC Chemical Class Fractions from the 700-750°F (A) and 750-800°F (B) Boiling Point Fractions of SRC-II Heavy Distillate Product

the protonated molecular ion of C_2-carbazoles. The homologous series of ions at m/z 194, 208, 222, 236, and 250 represent a series of alkylated phenanthridines, acridines and/or benzoquinolines. These two homologous series represent the most abundant species in this boiling-point chemical class fraction. Under the conditions of the experiment, 75°C and 360 bar (isobaric), compounds with molecular weights up to approximately 300 daltons eluted from the C_{18} column. The carbazole and phenanthridine series are also found to be important species in the mass spectrum of the 750-800°F boiling point cut (Figure 9B). Because the average boiling point is higher, we observed the most abundant alkylated carbazole at m/z 224, a shift of two methylene units higher than the most abundant carbazole homologue found in the 700-750°F fraction. The alkylphenanthridine series is now the most abundant homologous series in the spectrum. A third homologous series, at m/z 204, 218, 232, 246, and 260, is also important in this spectrum; it is probably composed of a series of alkylated azapyrenes and azafluoranthenes. Compounds with molecular weights up to about 320 daltons are observed in this spectrum.

The spectra shown in Figure 9 are representative of the type of information that can be obtained by direct-probe inlet mass spectrometry when the ionization conditions are chosen such that only molecular weight information is obtained. The use of a microbore chromatographic column enables additional information about a complex mixture to be obtained because of the chromatographic separation of components that results from the chemical and physical interactions of the components with the stationary phase of the column. This concept can be demonstrated by examining the individual mass spectra (or, in this case, scan-averaged mass spectra that are the averages of data acquired during a 0.5-min interval) acquired during the microbore SFC/MS analyses of the two SRC-II boiling-point cut chemical class fractions previously discussed. Figure 10 displays four averaged mass spectra that represent the components that eluted during the analyses of the 700-750°F SRC-II NPAC fraction during the time periods of 7.0 to 7.5 min (Figure 10A), 7.5 to 8.0 min (Figure 10B), 8.8 to 9.4 min (Figure 10C), and 9.5 to 10.0 min (Figure 10D). Figure 11 displays five averaged mass spectra that represent the components that eluted during the analyses of the 750-800°F SRC-II NPAC fraction during the time periods of 7.6 to 8.2 min (Figure 11A), 9.4 to 10.0 min (Figure 11B), 10.6 to 11.2 min (Figure 11C), 11.8 to 12.4 min (Figure 11D), and 13.0 to 13.6 min (Figure 11E).

Whereas the total ion chromatograms obtained for these analyses show a relatively featureless, rapid increase in intensity to a broad peak and a gradual decrease back to baseline, the individual spectra obtained during the elution show the changes in the chemical nature of the analytes being eluted.

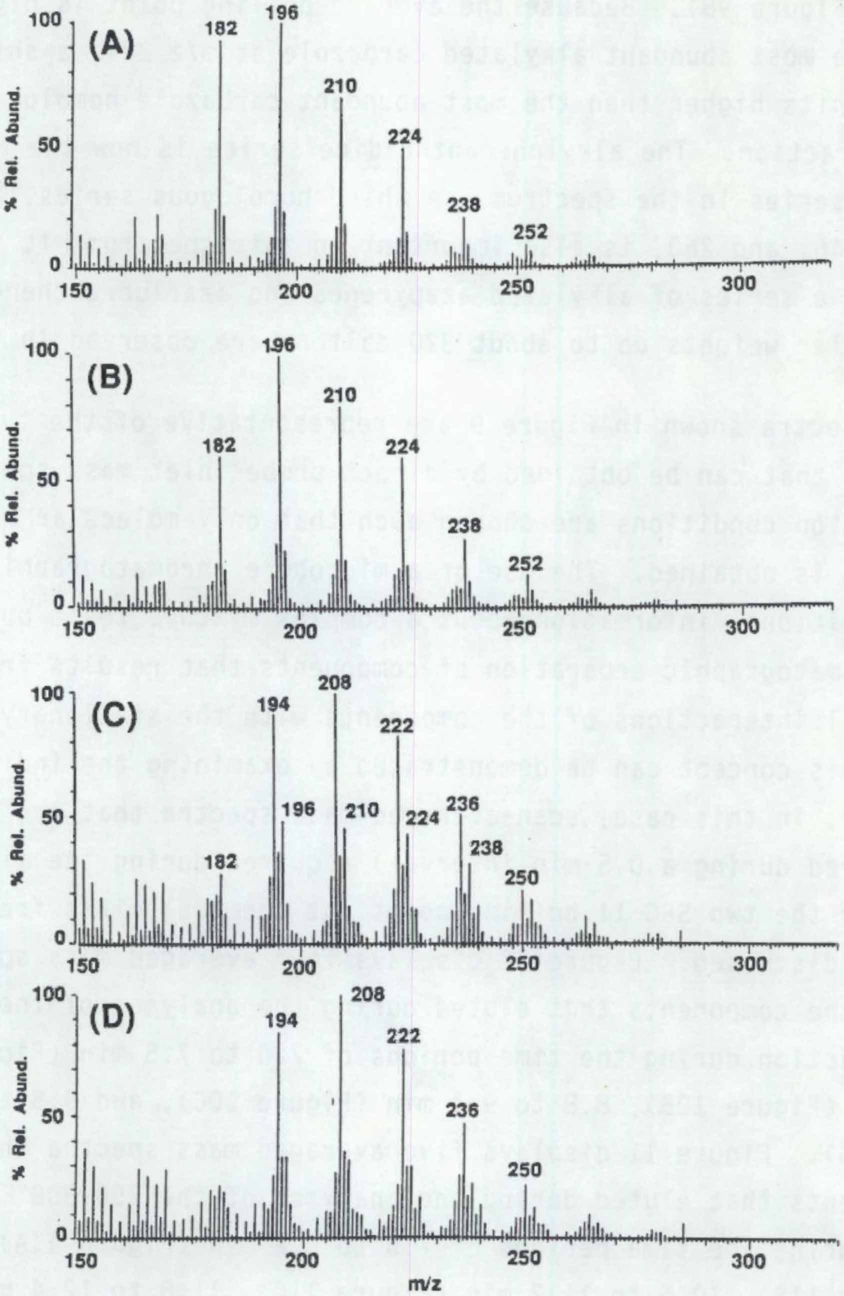

FIGURE 10. Mass Spectra from the Microbore SFC/MS Analysis of the NPAC Chemical Class Fraction, 700-750°F Boiling Point Fraction, SRC-II Heavy Distillate Product Averaged over the Acquisition Time Periods of (A) 7.0 to 7.5 min, (B) 7.5 to 8.0 min, (C) 8.8 to 9.4 min, and (D) 9.5 to 10.0 min

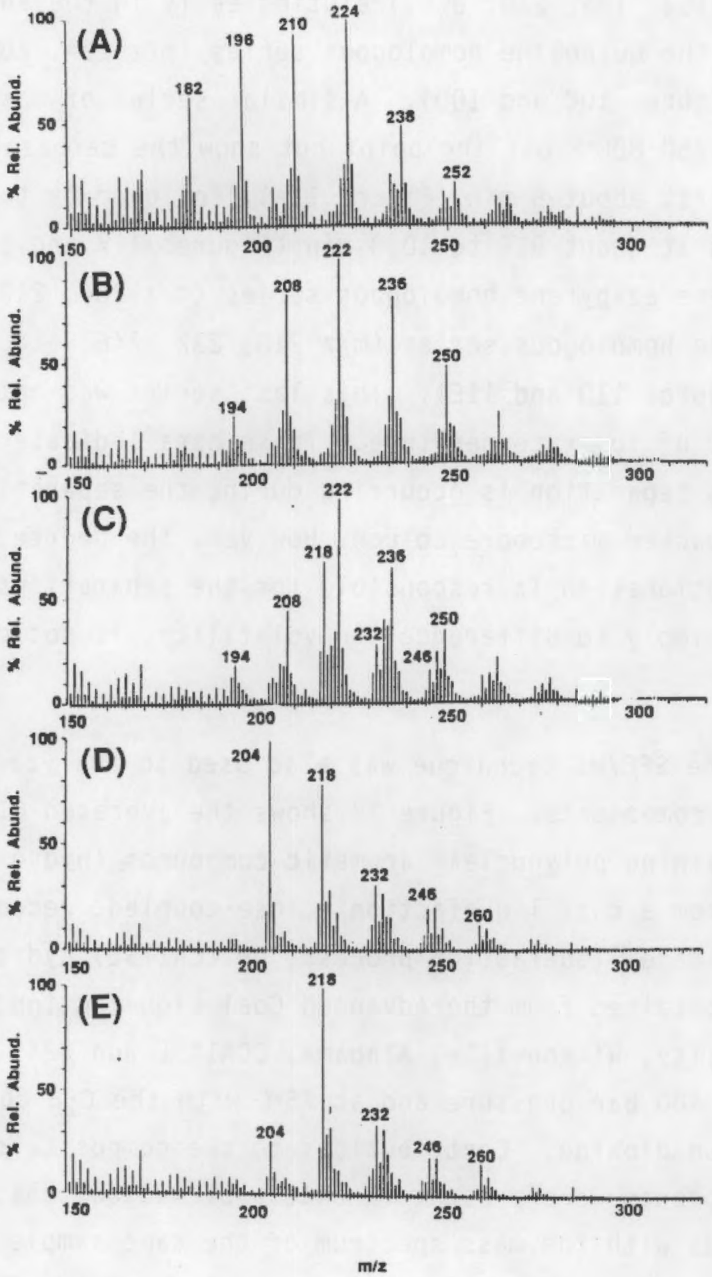

FIGURE 11. Mass Spectra from the Microbore SFC/MS Analysis of the NPAC Chemical Class Fraction, 750-800°F Boiling Point Fraction, SRC-II Heavy Distillate Product Averaged over the Acquisition Time Periods of (A) 7.6 to 8.2 min, (B) 9.4 to 10.0 min, (C) 10.6 to 11.2 min, (D) 11.8 to 12.4 min and (E) 13.0 to 13.6 min

For example, the spectra shown in Figure 10 show the carbazole homologous series (m/z 168, 182, 196, 210, etc.) eluting early in the analysis (Figures 10A and 10B) and the quinoline homologous series (m/z 194, 208, 222, etc.) eluting later (Figures 10C and 10D). A similar series of mass spectra, obtained for the 750-800°F boiling-point cut show the carbazole homologous series eluting first about 8 min (Figure 11A), followed by the quinoline homologous series at about 9.5 to 10.0 min (Figures 11B and 11C), followed by the azafluoranthene/azapyrene homologous series (m/z 204, 218, 232, etc.) and the benzocarbazole homologous series (m/z 218, 232, 246, etc.) eluting at about 12 min (Figures 11D and 11E). This last series was not observed in the boiling point cut of lower temperature. These data indicate that some degree of chemical class separation is occurring during the separation of the mixtures on the packed microbore column. However, the degree to which this mechanism of fractionation is responsible for the separations, relative to separations due simply to differences in volatility, is not currently understood.

The microbore SFC/MS technique was also used to analyze a mixture containing polar components. Figure 12 shows the averaged CI mass spectrum of the hydroxy-containing polynuclear aromatic compounds (hydroxy-PAC) chemical class fraction from a coal liquefaction (close-coupled, reconfigured, integrated, two-stage liquefaction process, or CCRITSL) hydrotreater unit feed stream material obtained from the Advanced Coal Liquefaction Research and Development Facility, Wilsonville, Alabama, CCRITSL run #249. The analysis was conducted at 400 bar pressure and at 75°C with the C_{18} column using 2% 2-propanol in carbon dioxide. Contributions to the composite spectrum arising from sample components were present in excess of 400 daltons. This spectrum favorably compares with the mass spectrum of the same sample acquired by low-voltage electron impact, probe inlet mass spectrometry (Wright 1987). The small gaps observed in the mass spectrum in Figure 12 (around m/z 194, 208, and 248) result because the presence of intense background ions arising from solvent clusters and column bleed prevented us from acquiring data in those mass windows.

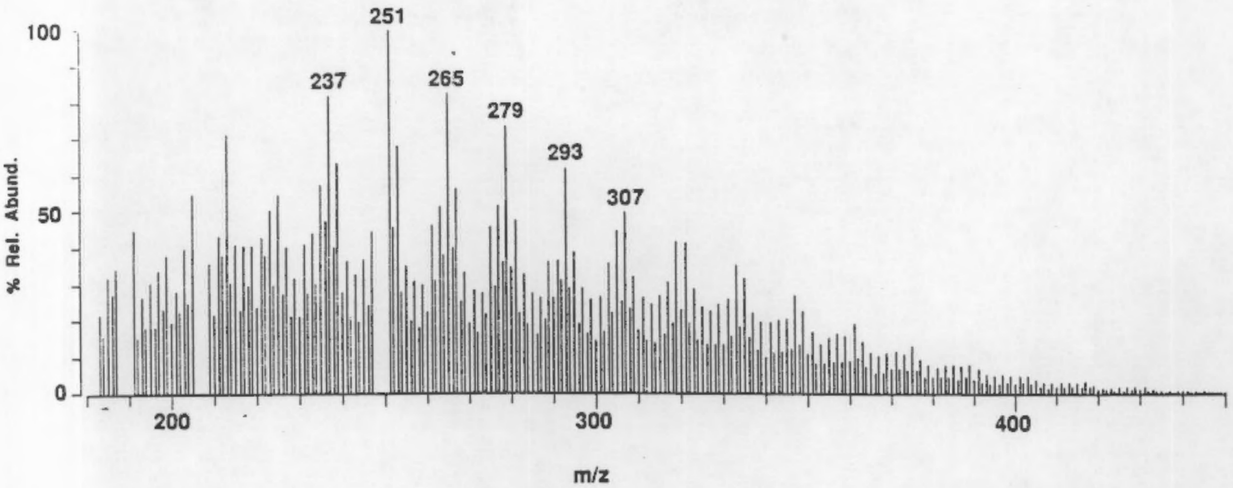

FIGURE 12. Scan-Averaged Mass Spectrum of the Hydroxy-PAC Chemical Class Fraction of a Hydrotreater Unit Feed from the CCRITSL Process

TECHNICAL OBJECTIVES FOR NEXT QUARTER AND BEYOND

The ability to obtain data on the polar hydroxy-PAC fraction and the slightly less-polar NPAC fractions by using the microbore column SFC/MS technique demonstrates the utility of this approach for the analysis of higher-molecular-weight and more-polar coal components. Results of these preliminary experiments have indicated future directions for work on this system, some which will be explored in the next quarter and throughout the next fiscal year. Included among these endeavors are: use of alternative HPLC-type stationary phases of varying chemical functionality to gain some additional selectivity in the analysis of complex mixtures, including samples of fossil fuels received from METC; use of other CI reagent gases to obtain additional chemical information on the samples; use of other polar fluids or fluid mixtures, such as CO_2-acetic acid, for microbore SFC/MS; and determination of factors that control transfer of higher-molecular-weight, more-polar and less-volatile materials through the HFR interface to the MS ion source. These factors may include the following: restrictor heater temperature, restrictor design and configuration, ion source and fluid expansion region temperatures, fluid temperature and pressure, stationary phase type, and fluid flow rate.

Other planned investigations include similar analyses on wider-bore (100 µm) capillary columns with thick stationary phase layers and with splitless injection using the HFR interface. These techniques would allow a greater sample loading for more dynamic range on a chromatographic column, with greater efficiency than would a packed column when a long packed column is used at a high fluid flow rate. The outcome could be improved separations, yielding more detail concerning the chemical nature of components in the complex mixture. We will attempt pressure-programmed separations of the complex mixtures on the microbore columns to improve the separations and to increase the information derived from each analysis. A longer-range goal is the use of triple-quadrupole tandem mass spectrometry following the microbore SFC/MS to obtain information on the chemical nature of samples or increase the specificity of microbore SFC/MS analyses.

Also proposed for the next quarter is a more-formal evaluation of the performance of the polished restrictors in comparison with other types of restrictors such as straight capillary restrictors, drawn restrictors, and frit restrictors. Each type will be tested with the same samples and under the same conditions to determine how well each performs at allowing transfer of higher-molecular-weight, more-polar materials with the use of modified supercritical fluids.

Plans have been made to construct a discharge ionization ion source for the mass spectrometer coupled to the HFR interface. This mode of ionization may aid in the transfer/ionization of materials of very low volatility. The evaluation of this ion source may begin next quarter, and other experiments requiring this instrumentation would then be postponed.

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