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SUPERCRITICAL FLUID CHROMATOGRAPHY/SUPERSONIC
JET SPECTROSCOPY

Progress Report for November 1, 1983—January 31, 1984

By
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Progress Report

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Prepared by

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SUMMARY

Modifications were made in the designs for the supercritical fluid extraction/fractionation unit and the vacuum chamber for supersonic jet spectroscopy. The construction of the extraction/fractionation unit is nearly complete and the construction of the vacuum system is presently underway.

An interface has been constructed for supercritical fluid chromatography - mass spectrometry based on direct fluid injection with provision for circulating a heated liquid for precise temperature control. Initial experiments indicate effective transfer of the chromatographic effluent, and preservation of chromatographic efficiency.

WORK PERFORMED

Supercritical Fluid Fractionation

During this period, a supercritical fluid extractor/fractionator was constructed according to the design shown in Figure 1. Some changes were made in the design presented in the last progress report. Instead of "down-programming" the pressure for selective precipitation, the new design utilizes pressure increases to selectively extract the sample under study. The sample is placed in the extraction vessel (C), which is nothing more than a short piece of 1/8" or 1/4" o. d. stainless steel tubing with micropore frits on each end. With valves 101-104 closed, the system is brought to the desired initial pressure by pumping the extraction fluid into the extraction vessel with the HPLC syringe pump (A). At this time also, the system is heated to the required supercritical temperature and allowed to equilibrate. Valve 101 is next opened and a quantity of solvent is pumped through the extraction vessel (C) and into vessel E1 where the first fraction is collected by maintaining the collection vessel (E1) at a lower pressure with nitrogen gas from a high pressure cylinder. At the lower pressure, the sample precipitates and the extraction solvent is vented through valve 202. To collect the next fraction, valve 101 is closed and the system pressure is increased to the next desired level. Valve 102 is then opened and a quantity of the extraction solvent is pumped into vessel E2, again held at lower pressure with N₂ as before. This process is then repeated to collect the final two fractions.

The supercritical fluid extractor/fractionator was constructed entirely of stainless steel. The syringe pump cylinder has a volume of 375 mL and each of the fraction collection vessels (E1-E4) holds approximately 150 mL. The system was designed for maximum flexibility (pressures and flow rates can be adjusted by varying restrictor dimension, the extraction vessel can be as large or as small as desired, and various packings may be used in the extraction vessel to improve the fractionation). An effort was also made to keep the system as simple as possible, while at the same time allowing changes to be made as needed.

At present, construction of the supercritical fluid extractor/fractionator is 90% complete. All that remains are the electronics for pressure control of the HPLC syringe pump and the electronics for the pressure transducers.

Mass Spectrometry

A temperature regulated interface between the supercritical fluid chromatograph and mass spectrometer was constructed as shown in Figure 2. Initial efforts involved resistance heating of the transfer line, which proved unsatisfactory. The end of the interface that was positioned in the mass spectrometer ion source was always at higher temperature than the rest of the interface because of less effective heat conduction. Since the distance between the chromatograph and MS is usually greater than for interfaces to other detectors, a temperature regulated interface is needed in order to keep the transfer line under supercritical fluid conditions. This is best accomplished by circulating a silicone fluid in tubing through the oven for heating,

then through a small auxillary heater to allow for more precise control of temperature, and finally through a jacket in the direct fluid inlet probe. At the end of the probe, a union is made to an appropriate capillary restrictor, which passes through a graphite ferrule into the probe nozzle. The end of the restrictor extends just to the end of the nozzle which is directed into the ion source region. The purpose of the nozzle is to allow for alignment in the ion source and to create a seal in order to maintain the high pressures needed for CI. The restrictor itself is a short length of very small-diameter fused silica (approximately 5-15 μm i.d.).

The interface construction is completed, and it is presently under evaluation. Figure 3 shows a total-ion-plot of a toxaphene sample. Toxaphene is a complex mixture resulting from chlorination of camphene. This chromatogram shows that the high chromatographic efficiency is maintained after passing through the interface. A more complete evaluation of the interface will be contained in the next progress report.

Supersonic Jet Spectroscopy

MDC Vacuum Products corporation is currently building a vacuum chamber for the supersonic expansion experiments. During the last quarter, and after having received several bids on our first proposed chamber, we made extensive modifications to our design (see Figure 4). The end result is not only a less expensive unit, but, we believe, a more versatile one, well-suited to the proposed work. In the meantime we have had several ports built for a small, temporary chamber for initial

experiments, which ports will be able to be transferred with only little modification to the larger system when it arrives.

We have obtained a GC oven and a high-pressure piston pump for supercritical fluid generation and are preparing to connect these to the small chamber so that preliminary experiments can be run on the effects of nozzle configuration and the importance of thermal insulation of the nozzle. Also being constructed are light baffles and mounts for the beam steering optics for the laser-induced fluorescence experiments. It is likely, however that the necessity for high rejection of scattered light will require much tighter light baffles than we plan to use in our initial work. Since, in that case, it will be easier to align the gas jet on the laser beam rather than vice versa, we have devised on paper an XYZ-translation mechanism for steering the nozzle, but we are holding off on its construction until we see whether the looser light baffling will be adequate.

One of the most critical parts in the coupled chromatograph/supersonic jet apparatus may be the interface between the oven and the vacuum chamber, in particular near the nozzle tip. Unlike other methods of detection such as fluorescence spectroscopy of a sample still in the supercritical fluid or mass spectrometry, the supersonic jet technique may be seriously affected by a drop in the temperature of the carrier fluid below the critical point before the nozzle tip; condensation of the solute would eliminate much of the spectral line-narrowing advantage of the supersonic expansion. Therefore, we suspect that previous interface designs are not sufficient for our needs, and we have given

careful consideration to alternate designs. Before proceeding to build any of the thermal probes which we have worked out, however, we wish to obtain results from tests described in the next section in order to establish just how critical thermal insulation near the nozzle tip is and to enable us to separate such thermal problems from nucleation effects due to nozzle geometry and backing pressure.

It is of some interest to be able to probe the expansion characteristics of the carrier fluid, but laser-induced fluorescence is not suitable for the common carrier fluids. The strong infrared transitions in CO_2 make infrared fluorescence measurements on this molecule feasible. We have therefore constructed a heat pipe as an alkali metal vapor, Raman downshifter¹ for our dye laser in order to have a tunable, coherent infrared source. We have been testing the heat pipe for vacuum leaks and putting together an associated gas handling manifold. We expect to put the heat pipe into operation shortly.

Unfortunately we have been short-handed during the last few months, but we have spent some time seeking and interviewing post-doctoral candidates, and will have a post-doctoral research associate join our group presently who will devote full time to the supersonic jet project.

WORK PROPOSED FOR NEXT PERIOD

The extraction/fractionation unit will be evaluated using standard polycyclic aromatic compounds and coal liquids. Both chemical class fractionation and size separation will be addressed.

Initial experiments will involve the use of CO_2 as the supercritical fluid, although other fluids are of interest and will eventually be evaluated.

A rigorous evaluation of the SFC-MS interface will be done. Both electron impact and chemical ionization modes will be compared with similar results obtained from capillary gas chromatography.

We are still working on nozzle designs and construction techniques, focusing first on throughput characteristics of the nozzles and structural integrity. We have made several crude calculations modelling supersonic expansions in order to determine the best conditions and nozzle geometries, but these attempts at modelling the jet, while helping to highlight the parameters which are important, have contained too many unknowns to yield definitive results. We plan to attempt a more rigorous model of the expansion of CO_2 , including a real state description of the fluid from supercritical to gas phase.

Certain information can only be obtained through experiment, however. Among the first investigations we wish to make is a comparison of the jet spectrum of benzene obtained when it is seeded into subcritical, liquid CO_2 , and those of benzene in gaseous CO_2 and helium. These experiments should help to answer questions about the importance of thermal insulation of the nozzle and to better understand results for expansions of supercritical CO_2 .

We also hope to attempt to monitor the expansion of the CO_2 directly via spatially resolved infrared fluorescence. The heat pipe must be put into operation for this work, and

an infrared detector and filters obtained.

We hope to accomplish much of the above work with the small vacuum chamber, but we intend to continue preparations for the larger chamber, including devising a supporting framework for the entire apparatus and setting up the necessary power, cooling, and pressure monitoring equipment.

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Fig. 1 Schematic Diagram of Supercritical Fluid Fractionation Equipment. Key: (A) HPLC Syringe Pump with Pressure Control, (B) Chromatographic Oven, (C) Extraction/Fractionation Vessel with micropore frits on each end, (D) Solvent Preheater/Equilibrator, (E1-E4) Fraction Collection Vessels, (101-104) High temperature valves, (201-209) Inert Gas Valves, (RV) Pressure Relief Valve, (CV) Check Valve, (P) Pressure Indicator, (M) Fused Silica Restrictor

Fig. 2 Schematic diagram of the SFC-MS interface

Fig. 3 Total-ion-plot of a Toxaphene sample. Conditions: 20 m x 75 μ m i.d. fused silica column; 50% phenyl polysiloxane stationary phase (0.50 μ m film thickness); n-pentane mobile phase at 210 $^{\circ}$ C; pressure program from 30 to 36 atm at 0.25 atm min $^{-1}$ after an initial 5-min isobaric period; mass spectrometer scanned from 120 to 500 amu at 137 amu s $^{-1}$.

Fig.4 Diagram of revised design for the supersonic expansion chamber showing (left) a side view and (right) a view from the right side.