



## Project Summary

# Supercritical Fluid Extraction of Particulate and Adsorbent Materials

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The applicability of supercritical fluid extraction of semivolatile and heavier molecular weight compounds from adsorbents and particulate materials was investigated. These studies included off-line supercritical fluid extraction, direct supercritical fluid extraction-mass spectrometry, and on-line supercritical fluid extraction-gas chromatography. A related study on the development of fluorescence detection for capillary supercritical fluid chromatography (SFC) was also conducted.

Gram quantities of spiked XAD-2 resin, SK-4 carbon, polyurethane foam (PUF), and NBS Urban Dust particles were subjected to off-line extraction, using carbon dioxide, pentane, 20 mole percent methanol in carbon dioxide, and 20 mole percent ethanol in pentane as supercritical fluid extracting solvents under a variety of conditions. The supercritical fluid extractions were more rapid than Soxhlet extractions, but similar extraction efficiencies were obtained. Different extraction recoveries were obtained with the various fluids. Evidence suggests that much better recoveries could be obtained if the collection procedures were modified to eliminate volatilization and aerosol formation after extraction. More rapid extraction procedures also appear feasible.

Direct supercritical fluid extraction-mass spectrometry allowed the extraction profiles for each model compound from the XAD-2 resin to be obtained as a function of time. The compounds displayed different threshold pressures at which extractability was detected and widely varying decay curves as the material was removed.

To develop methods to eliminate or minimize sample preparation procedures,

studies using on-line supercritical fluid extraction-gas chromatography were conducted. With this methodology, milligram quantities of samples such as particles or adsorbents were selectively extracted using supercritical carbon dioxide at various pressures, followed by capillary gas chromatographic analysis of each extract. The technique was applied to the NBS Urban Dust particles to demonstrate that selective and direct analyses could be obtained.

To obtain high detection sensitivity for SFC using fluids that are incompatible with flame ionization detection, development of reliable capillary SFC fluorescence detection was also undertaken. The necessary modifications of a commercial HPLC fluorescence detector were completed and successfully interfaced to an SFC instrument using supercritical pentane as a mobile phase. The model compounds from the extraction studies were used to demonstrate successful chromatographic separation and fluorescence detection.

*This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Numerous methods and combinations of methods with varying degrees of complexity are currently employed to prepare samples for analysis. Less complex, more rapid, and more sensitive preparation procedures would be desirable in many cases, particularly for small samples or low con-

centrations of analytes. Supercritical fluid extraction procedures are attracting attention for use in selective large-scale process applications, but only limited attention has been given to using supercritical fluid extraction methods in analytical applications. The goals of this study were to determine the potential utility of supercritical fluid extraction for analytical sample preparation and to develop improved methods of analysis utilizing these procedures.

The potential advantages of supercritical fluid extraction accrue from the properties of a solvent at temperatures and pressures above its critical point. At elevated pressure this single phase will have properties that are intermediate between those of the gas and liquid phases and are dependent upon the fluid composition, temperature, and pressure. The compressibility of supercritical fluids is large just above the critical temperature; at this point small changes in pressure result in large changes in the density of the fluid. Figure 1 shows a typical pressure-density relationship in terms of reduced parameters (e.g., pressure, temperature, or density divided by its respective critical parameter). Isotherms for various reduced temperatures show the variations in density that can be expected with changes in pressure. Thus, the density of a supercritical fluid will be typically  $10^2$  to  $10^3$  times greater than that of the gas. Consequently, molecular interactions increase due to the shorter intermolecular distances. However, the diffusion coefficients and viscosity of the fluid remain similar to that of the gas. The "liquid-like" behavior of a supercritical fluid results in greatly enhanced solubilizing capabilities compared to a subcritical gas, but with higher diffusion coefficients, lower viscosity, and an extended temperature range compared to the corresponding liquid. These properties allow solvent strengths similar to those of liquids and the potential for more rapid extraction rates than are possible with liquids.

## Procedure

Various studies were conducted to evaluate the applicability and efficiency of analytical supercritical fluid extraction methods. These investigations were among the very first to specifically address the use of supercritical fluid extraction for analytical purposes. Consequently, little related information exists. The studies involved in this project included offline supercritical fluid extraction of adsorbents and particles, direct supercritical fluid extraction-mass spectrometry, and on-line

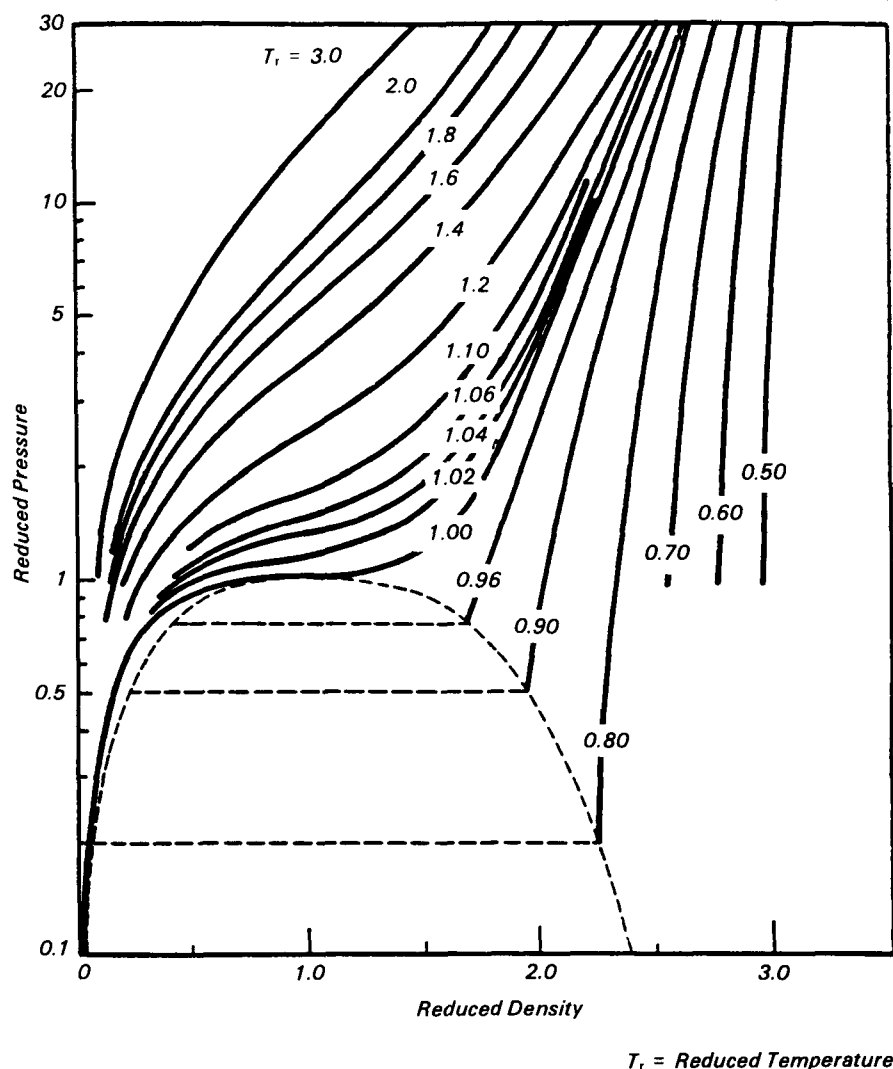


Figure 1. Typical pressure-density behavior of a pure supercritical fluid.

supercritical fluid extraction-gas chromatography. A fluorescence detection supercritical fluid chromatography (SFC) system was also developed. Gram quantities of XAD-2 resin, SK-4 carbon and polyurethane foam (PUF) were spiked with selected large polycyclic aromatic compounds and subjected to supercritical fluid extraction using either carbon dioxide, a carbon dioxide-methanol mixture, pentane, or a pentane-ethanol mixture as extracting fluids. NBS Urban Dust (SRM 1649) was also subjected to the same extraction conditions. The extraction efficiency as a function of the extracting fluid was evaluated. Traditional liquid Soxhlet extractions of the same matrices were conducted and compared to the supercritical fluid extractions. Preliminary extractions using direct supercritical fluid extraction-

mass spectrometry were also conducted to obtain individual extraction profiles as a function of time for each of the spiked compounds. Direct analysis methods, in which sample preparation and analysis are combined, were investigated using on-line supercritical fluid extraction-gas chromatography with the NBS Urban Dust as a sample matrix. Fluorescence SFC detection was developed to provide high detection sensitivity using supercritical fluid systems that are not compatible with flame ionization detection.

## Results

High molecular weight polycyclic aromatic compounds at ppm concentrations were extracted from typical adsorbent matrices using supercritical fluid extraction methods. The various fluids displayed

different extraction strengths, with carbon dioxide generally being the poorest and the alcohol-modified mixtures the best extracting fluid systems. Supercritical fluid extraction provided relatively fast extractions (1-2 hr or less) compared to traditional Soxhlet extraction.

Of the fluids studied, the carbon dioxide-methanol mixture and pentane gave the best extraction recoveries from the XAD resin. Carbon dioxide alone at 50 °C was a poor extraction solvent. Under the experimental conditions used, Soxhlet extraction with methylene chloride gave better extraction recoveries than did carbon dioxide.

All the supercritical fluid and Soxhlet extractions gave poor recoveries from the activated carbon. Of the supercritical fluids used with this matrix, the pentane-ethanol fluid system gave the best overall results. Soxhlet extraction after supercritical fluid extraction gave higher extraction recoveries than Soxhlet extraction before supercritical fluid extraction.

Difficulties were encountered with polyurethane foam, since it was soluble in the supercritical fluids. However, comparable extraction efficiencies were achieved with both carbon dioxide-methanol and pentane fluid systems compared to Soxhlet extraction with methylene chloride. Carbon dioxide at 50 °C was a poor extraction solvent for use with PUF.

The pentane-ethanol fluid system gave the highest recovery of material with the best extraction efficiency from the Urban Dust. Carbon dioxide at 50 °C and pentane at 210 °C gave poor extraction recoveries. Additional material was extracted by Soxhlet extraction with methylene chloride following supercritical fluid extraction.

In most cases higher extraction efficiencies (recoveries) were obtained with Soxhlet extraction than with supercritical fluid extraction. However, there was a problem with the collection of the supercritical fluid extracts, and a large percentage of material was lost due to aerosol formation. Unfortunately, this problem was not discovered until after completion of the work discussed above. Preliminary results using a collection system in which the total extraction effluent was trapped by freezing in a sealed vessel cooled in liquid nitrogen indicate that comparable extraction efficiencies can be obtained with both supercritical fluid and Soxhlet extraction.

## Conclusions and Recommendations

Direct supercritical fluid extraction-mass spectrometry provides a valuable means of simultaneously monitoring the extrac-

tion kinetics and threshold pressures for a number of compounds. An understanding of these parameters is necessary to obtain selective fractionation of complex samples.

On-line supercritical fluid extraction-gas chromatography provides a means of eliminating sample preparation and allows automated extraction and analysis of organic matrices. By utilizing the variable solvating power of supercritical fluids, selective extractions can be achieved.

Several recommendations can be made. The off-line supercritical fluid extraction studies should be repeated using the improved collection system (e.g., freezing the extraction effluent in a sealed flask cooled in liquid nitrogen) to prevent recovery losses. These results would be more meaningful than the existing data in terms of comparing extraction efficiencies between the various fluid systems and to Soxhlet extractions.

Spiked adsorbents and particulate samples should be subjected to supercritical fluid extraction after Soxhlet extraction to determine if additional material can be recovered. Larger volumes of the supercritical extraction fluids (>250 mL liquid volume) should be utilized to determine if more complete extraction can be obtained. Methods of enhancing extractability by recycling the fluid or improving fluid contact with the sample matrix should be investigated. Work on direct supercritical fluid extraction-mass spectrometry should be continued using isobaric conditions to obtain extraction kinetics data. These data would be useful for defining the optimum conditions to selectively extract specific compounds from a complex matrix.

The on-line supercritical fluid extraction-gas chromatography methodology should be applied to additional sample matrices, and investigations should be conducted to answer questions concerning quantitative methods. Extraction kinetics could also be studied using the instrumentation.

The fluorescence detection supercritical fluid chromatography instrumentation should be evaluated for quantitative analysis and applied to the nonvolatile materials in the model compound mixture. The applicability of supercritical fluid chromatographic analysis to other nonvolatile materials with fluorescent properties should also be investigated.

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*Nancy K. Wilson is the EPA Project Officer (see below).*

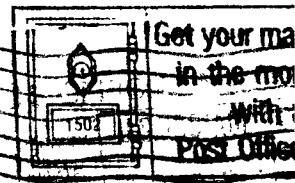
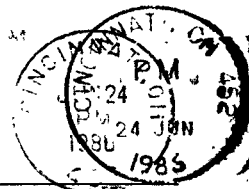
*The complete report, entitled "Supercritical Fluid Extraction of Particulate and Adsorbent Materials," (Order No. PB 86-175 999/AS; Cost: \$11.95, subject to change) will be available only from:*

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