



Project Summary

Supercritical Fluid Extraction of Particulate and Adsorbent Materials: Part II

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Supercritical fluids have solvent strengths similar to those of liquids, but have higher diffusion coefficients, lower viscosities and an extended temperature range which provides the potential for more rapid and efficient extraction than can be achieved with liquids. In this project, the applicability and efficiency of analytical supercritical fluid extraction and related methodologies were evaluated. These studies included development of quantitative off-line supercritical fluid extraction methodology and a comparison to traditional Soxhlet extraction, the development and evaluation of on-line supercritical fluid extraction-gas chromatography for combined sample preparation and analysis, and direct supercritical fluid extraction-mass spectrometry for the monitoring of specific extraction profiles as a function of time. The sample matrices included an air particulate sample, XAD-2 resin, polyurethane foam (PUF), and Spherocarb®* adsorbent, which were spiked with various model compounds. Carbon dioxide, isobutane, and methanol-modified (18.2 mole %) carbon dioxide were used as supercritical fluid systems. The quantitative analysis capability of a fluorescence detection supercritical fluid chromatography method and solute focusing methods for capillary supercritical fluid chromatography were also developed and evaluated.

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 concentrations of analytes. Supercritical fluid extraction (SFE) has been successfully used for several large-scale chemical processing applications and is currently attracting renewed interest. However, only limited attention has been given to SFE methods for analytical applications. A number of advantages including more rapid extraction rates, more efficient extractions, increased selectivity, combined analyte fractionation in conjunction with extraction, and direct continuous on-line analysis, such as with mass spectrometry or periodic gas chromatographic analysis, are possible with SFE compared to conventional liquid extraction methods. The goals of this study were to determine the potential utility of SFE for analytical sample preparation and to develop improved methods of analysis utilizing these and other supercritical fluid analytical methodologies.

The potential advantages of SFE accrue from the properties of a solvent

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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 depend on the fluid composition, pressure, and temperature. The compressibility of supercritical fluids is large just above the critical temperature, and small changes in pressure result in large changes in density of the fluid. The density of a supercritical fluid is typically 10^2 to 10^3 times greater than that of the gas. Consequently, molecular interactions increase due to shorter intermolecular distances. However, the diffusion coefficients and viscosity of the fluid, although density-dependent, remain similar to those of a gas. The "liquid-like" behavior of a supercritical fluid results in enhanced solubilizing capabilities compared to the subcritical gas, and in 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 but with greatly improved mass transfer characteristics, which provide the potential for both more rapid extraction rates and more efficient extraction due to better penetration of the matrix.

Procedure

Studies were conducted to evaluate the applicability and efficiency of analytical SFE and related methodologies. These studies included off-line SFE of adsorbents and particles, on-line supercritical fluid extraction-capillary gas chromatography (SFE-GC), and direct supercritical fluid extraction-mass spectrometry (SFE-MS). The quantitative analysis capability of the fluorescence detection supercritical fluid chromatography (SFC) system that was previously developed in this project was also evaluated. Preliminary studies aimed at developing solute focusing methods for capillary SFC similar to cryogenic trapping in gas chromatography were also conducted.

In the off-line SFE studies, various fluid systems were evaluated and compared to Soxhlet extraction for the recovery of low concentrations (ppm) of model compounds from selected adsorbents. Higher molecular weight (228-450 daltons) polycyclic aromatic hydrocarbons (PAH) were extracted from XAD-2 resin, polyurethane foam, and Spherocarb® adsorbents. Air particulate matter was also used as a complex matrix for evaluation of the SFE methods. In

addition to carbon dioxide, isobutane and methanol-modified (18.2 mole percent) carbon dioxide were used for SFE solvents. Instrumentation was designed to allow extraction of gram quantities of the matrix at pressures up to 400 bar and temperatures up to 235°C, with collection of the effluent in a sealed liquid-nitrogen-cooled flask.

A logical extension of SFE is to combine the process with a chromatographic analysis method. The variable solvating power of a supercritical fluid furnishes the mechanisms for the selective extraction of the components of interest from the sample matrix and provides the basis for an automated method where sample preparation and analysis can be instrumentally linked. Instrumentation and methodology were developed for the automated SFE-GC system. The supercritical fluid extracts were decompressed through a restrictor to deposit and concentrate the analytes at the inlet of a standard capillary gas chromatography column for subsequent analyses. This methodology allows several modes of operation including quantitative extraction of all analytes from a sample matrix, quantitative extraction and concentration of trace analytes, selective extractions at various solvating powers to obtain specific fractions, and multiple-step extractions at various pressures for qualitative characterizations. These modes of operation were developed, and the potential utility of this methodology for sample extraction and selective fractionation was demonstrated using a standard polycyclic aromatic hydrocarbon mixture and two complex sample matrices.

Direct SFE-MS was used to monitor the individual extraction of each model compound as it was extracted from XAD-2 resin, PUF, and Spherocarb® adsorbents with carbon dioxide, isobutane, and methanol-modified (18.2 mole %) carbon dioxide fluid systems. Individual extraction profiles of each of the spiked compounds as a function of time were obtained, and the different extraction behaviors (threshold pressures, extraction rate, solubility, decay curves, etc.) of the model compounds from the various adsorbents were observed.

A fluorescence detection capillary SFC system was developed to obtain high sensitivity detection when using fluids that are not compatible with flame ionization detection, and its quantitative analysis capability was evaluated. These procedures included evaluation of a

multi-level detector calibration of several compounds, documentation of the reproducibility of multiple determinations of specific mixtures, and comparison of the quantitative values obtained from parallel determinations using this methodology and capillary gas chromatography.

Preliminary studies were conducted to develop solute focusing methods for capillary SFC similar to cryogenic trapping in gas chromatography. One approach that proved moderately successful was to create density gradients within a short length of the column by altering the fluid temperature.

Results

Optimized off-line analytical SFE instrumentation and methods were developed that allowed high molecular weight polycyclic aromatic compounds to be successfully extracted and recovered from the adsorbent matrices. A reciprocating pump provided the potential for use of unlimited volumes of fluid in an extraction, and collection of the extraction effluent in a sealed liquid-nitrogen-cooled flask prevented analyte losses due to aerosol formation during fluid decompression. When an open collection method was used under conditions where aerosol formation was expected to be inhibited (low temperature expansion where a two-phase product was expected or utilization of a polar liquid-modified fluid), significantly higher extraction recoveries were obtained. The model compounds were more easily extracted from PUF than from XAD-2 resin. Higher levels of background components were also extracted from PUF, and the PUF itself appeared to be slightly soluble in methanol-modified carbon dioxide. Except for PUF, the various adsorbents did not appear to be affected by SFE. Supercritical fluid extraction of the highly adsorptive Spherocarb® matrix with isobutane and with methanol-modified carbon dioxide fluids provided more efficient extraction recoveries than those achieved by Soxhlet extraction. However, only low levels of the less polar analytes were recovered. Supercritical fluid extraction also provided more rapid and improved extraction efficiency of PAH from Urban Dust than did Soxhlet extraction. The concentrations of selected compounds obtained from these analyses exhibited surprisingly good agreement with the NBS certified values.

On-line SFE-GC provides potential for combined sample preparation and anal-

ysis. In addition to completely automated operation, rapid analyses and high sensitivities can be achieved with this methodology. The selectivity obtainable with the wide range of solvent powers available with SFE provides the potential for fractionation of complex samples and isolation of specific analytes from a matrix. The quantitative extraction and transfer of PAH analytes from an XAD-2 resin to the gas chromatographic column for analysis was demonstrated. Quantitative extraction and transfer is dependent on solute solubility which requires using an adequate volume of the supercritical fluid.

Direct SFE-MS provides a means of simultaneously monitoring the extraction profiles of the individual model compounds from the adsorbents. The extraction behavior of the model compounds from the various adsorbents with the different fluid systems was consistent with the off-line SFE studies. The compounds were more soluble and better extractability was achieved with isobutane than carbon dioxide. More rapid exhaustion of the compounds was also obtained with isobutane. The methanol-modified carbon dioxide mixture was used under subcritical temperature conditions which resulted in a two-phase liquid-gas mixture rather than a supercritical fluid. Consequently, the polar compounds capable of hydrogen bonding with liquid methanol were extracted more rapidly and more efficiently than the neutral compounds. The model compounds were all extracted more easily from PUF than from XAD-2 resin with all the fluid systems studied. The extraction profile intensities from PUF correspond to the expected solubility orders of the compounds. The model compounds were so strongly adsorbed by SpheroCarb® that SFE-MS extraction profiles could not be obtained.

Linear response of the neutral PAH model compounds was achieved over the narrow concentration range studied, and sensitivities in the low picogram range were obtained using fluorescence detection SFC. Calibration plots with less than an 8% standard error were constructed from replicate analyses at four concentration levels. Slightly better calibration was obtained from peak heights than from peak areas. Replicate analyses of standard mixtures and authentic sample extracts agreed to within approximately 15%. Quantitative determinations of authentic sample extracts from parallel analyses using capillary gas chromatog-

raphy and fluorescence detection SFC were generally consistent within a 20% range. A significant portion of the quantitative variance can be attributed to problems associated with the injection method.

A moderately successful solute focusing technique for capillary SFC was developed. The technique used a local zone of lowered fluid density created by heating a short length of the column inlet. Preliminary evaluations of other approaches using a retention gap and a pressure gradient were also conducted.

Conclusions and Recommendations

Essentially quantitative recoveries of all the model compounds from the XAD-2 and PUF adsorbents were achieved by Soxhlet extraction. In general, the SFE methods provided extraction efficiencies comparable to traditional Soxhlet methods, but with over an order of magnitude increase in extraction speed. Supercritical fluid extractions were accomplished in 30-45 minutes compared to 16 hours for Soxhlet extraction. The more polar and higher molecular weight analytes were more difficult to extract from the adsorbents, and the methanol-modified carbon dioxide fluid and higher critical temperature isobutane systems provided higher extraction efficiencies than did carbon dioxide alone. Limited solubility of the higher molecular weight materials in carbon dioxide limited their recoveries with the relatively small volumes of fluid that were used.

The utility of on-line SFE-GC, and its qualitative operation for sample extraction from adsorbent matrices, and its potential for fractionation and isolation of specific components from complex matrices was demonstrated.

Direct SFE-MS allowed the individual extraction profile of each model compound to be monitored as it was extracted from XAD-2 and PUF adsorbents with carbon dioxide, isobutane, or methanol-modified (18.2 mole %) carbon dioxide. Extraction profiles for SpheroCarb® could not be constructed since only very low signal levels were detected.

The fluorescence detection SFC system was able to provide reliable quantitative determinations with a combined uncertainty of approximately 15%.

Several recommendations for off-line SFE studies can be made. Since the overall SFE rates appear to be limited by the solubility of the analytes in the

extraction fluid rather than by desorption or mass transfer rates, more rapid and more efficient extractions should be feasible by use of larger fluid volumes at higher rates. The use of higher fluid volumes may be best obtained by recompression and recycling of the fluid. Additional studies should be conducted to develop collection methods that can be routinely applied. A more rigorous study of the chemical composition of the supercritical fluid extracts of NBS Urban Dust should be conducted. Detailed fractionations and analyses of the extracts would not only provide additional chemical composition information, but would provide additional insights on the extraction process.

The on-line SFE-GC and SFE-MS extraction studies should be expanded. More rigorous quantitative studies using multiple analyses and a multi-level calibration with a variety of model compounds should be conducted to verify the performance of the on-line SFE-GC methodology. Methods of increasing the extraction fluid flow rate to allow extraction of larger sample matrices in a short time-frame should be investigated. The methanol-modified carbon dioxide SFE-MS studies should be repeated using an extraction temperature above the critical point and the results compared to those obtained in this study using a subcritical two-phase mixture. Appropriate response factors and quantitative SFE-MS extraction profiles should be obtained. The SFE-MS approach should be expanded to include a chromatographic separation step to allow concentration of trace components in the extraction effluent and to provide separation of the components prior to MS analysis.

The linearity of the fluorescence detector response should be evaluated over a much wider range, e.g., $>10^3$. Improved splitless injection methods should be developed to improve the accuracy and reproducibility of quantitative SFC analyses. Such improvements could include high-speed valve switching to effect lower volume injections and use of long retention gaps (>10 m) to aid solute focusing on the analytical column. The use of valves with 1/32" zero-dead-volume outlet fittings should also be investigated.

The development of on-column solute focusing methods for capillary SFC should be continued. This development should include use of long retention gaps coupled with thermal focusing and use of on-column solute concentration

methods employing extraction-injection
and pressure focusing techniques

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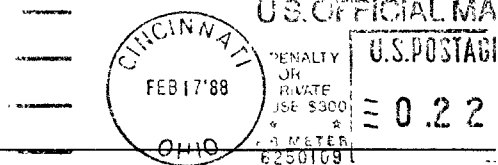
*The complete report, entitled "Supercritical Fluid Extraction of Particulate and
Adsorbent Materials: Part II," (Order No. PB 88-133 699/AS; Cost: \$14.95,
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