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Project Summary

Supercritical Fluid Chromatography for High Molecular Weight Organic Analysis

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This report describes a preliminary application of supercritical fluid mass spectrometry (MS) techniques developed at Battelle-Northwest to the analysis of a middle distillate fuel, an emission particulate extract, and the emission particulates themselves. These techniques include capillary column supercritical fluid chromatography (SFC) (alone) and coupled with MS, direct fluid injection (DFI)/MS, and supercritical fluid extraction (SFE)/MS. These techniques are still in an early stage of development, but have demonstrated considerable potential for difficult analytical problems. The present work demonstrates the feasibility of achieving high resolution separations of complex mixtures with SFC using nonpolar CO_2 as the mobile phase. Additionally, these analyses have provided an evaluation of the limitations of the present detector interfaces, resulted in further design improvements, and emphasized research areas for further investigation. The present work also demonstrates that SFC/MS application to complex mixtures can provide good separations and usable mass spectra. DFI/MS using supercritical ammonia was used to provide an efficient method of transporting sample components to the ionization source to obtain accurate molecular weight distribution data and structural information for rapid analysis of materials for which suitable separations have not yet been developed. Finally, high molecular species up to mass 1400 amu were detected during SFE/MS of the emission particulates using supercritical ammonia. The necessary research required to elevate the various supercritical fluid methods to routine application is summarized.

This Project Summary was developed by EPA's Air and Energy Engineering Research 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).

Summary

This report describes and summarizes an initial application of supercritical fluid analytical techniques for the analysis of complex mixtures. These techniques are capillary column SFC/MS, DFI/MS, and SFE/MS. These techniques are all in a relatively early stage of development, but show significant promise for application to previously intractable problems or for considerable simplification of established methodologies. The advantages of these techniques include greatly enhanced chromatographic resolution compared to high performance liquid chromatography (HPLC) and improved operation and compatibility with MS.

The present work demonstrates the feasibility of achieving high resolution separations of complex mixtures of moderate molecular weight (e.g., middle distillate fuel) samples using capillary column SFC and nonpolar CO_2 as the mobile fluid. Flame ionization detec-

tion (FID) was also employed and provided an efficient form of detection. Significant components of even the more polar nitrogen-containing polycyclic aromatic hydrocarbons and the hydroxylated polycyclic aromatic materials were successfully chromatographed. Coupled capillary column SFC/MS also proved to be successful for the analysis of the middle distillate fuel. Although the separation efficiency was somewhat less with MS detection, design improvements were earmarked which will greatly improve the interface performance and produce results comparable to FID. Chemical ionization (CI) mass spectra were also obtained for selected components in the middle distillate fuel. In order to elute high molecular weight nonvolatile compounds, further improvements in the chromatographic interface are necessary and the use of more polar fluid systems needs to be developed. The use of polar fluid systems necessitates expanded development of compatible capillary cloumn technology. The present work also demonstrates the utility of DFI/MS for the introduction of sample solutes to the mass spectrometer. These techniques can provide the basis for new rapid analysis methods, particularly in conjunction with tandem MS techniques (e.g., MS/MS). Essentially, any solute that is soluble in the supercritical fluid is transported to the ion source in DFI/MS. In this work, supercritical ammonia was used to transport and obtain CI spectra of the middle distillate fuel, chemical class fractions of the fuel, and of the emission particulate extract. Since these are complex mixtures the spectra were also complex, but molecular weight distribution data and some structural information were obtainable. MS/MS methods and/or high resolution MS would greatly aid in the interpretation of these such spectra for detection of particular components of interest. Finally, DFE/MS of the emission particulate sample with polar ammonia demonstrated that material up to mass 1400 amu were extractable. It appears that the DFI-MS method can be expanded to higher m/z values. The ma spectra which were obtained are co plex and additional investigation an t use of expanded techniques such MS/MS or high resolution MS will necessary to fully exploit this techniq

The present work clearly demo strates the promising potential of S and SFC/MS techniques for enhanc analytical characterization of "difficu samples. Further research will increa the utility of these methods as an e panded base of understanding and fined instrumentation are developed.

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The complete report, entitled "Supercritical Fluid Chromatography for High Molecular Weight Organic Analysis," (Order No. PB 87-110 524/AS; Cost: $13.95, subject to change) will be available only from:
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