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### Direct Mass Spectrometric Analysis of Supercritical Fluid Extraction Products

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## Direct Mass Spectrometric Analysis of Supercritical Fluid Extraction Products

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### Abstract

A method is described for the direct mass spectrometric analysis of the products of supercritical fluid extraction processes. A sample placed in an extraction cell is pressurized to supercritical conditions with a high pressure pump. The extracted products are continuously analyzed by direct fluid injection of a small sample ( $<50 \mu\text{L}/\text{min}$ ) into a mass spectrometer chemical ionization ion source. The extraction process can be observed as a function of pressure to determine "threshold pressures" for individual solutes or as a function of temperature at constant pressure for nonisothermal kinetic studies. The method is demonstrated for a supercritical fluid extraction of a bituminous coal using a *n*-pentane-isopropanol mixture at  $280^\circ\text{C}$  and pressures of 10 to 100 atm.

### INTRODUCTION

The last decade has seen a dramatic growth in the application of supercritical fluid extraction methods to a variety of areas (1, 2). The strong and often selective solvating power of supercritical fluids under controlled conditions (1, 3) can often provide for the extraction of specific compounds [e.g., caffeine from coffee (1)] as well as efficient extraction of a wide range of compounds under more severe conditions. Under more extreme conditions the "extraction" process is undoubtedly a combination of chemical reactions resulting in breakdown of a complex matrix combined with the extraction-distillation process of the supercritical fluid. In some cases it may be possible

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to use the reaction chemistry to particular advantage for modification of "extracted" products. Such systems may be extremely important in the development of synthetic fuels from solid fossil fuels, for example. The potential importance of these methods has been underlined by recent reviews describing the range of applications (1, 2).

A major deficiency in the development of supercritical fluid extraction (SFE) processes for a given application is related to the difficulty in direct and continuous analysis of high pressure and, sometimes, high temperature fluids. In particular, the desired analysis method should be selective, sensitive, and applicable to all extracted compounds and should not disrupt the process. Previous attempts at direct supercritical fluid analysis using mass spectrometry (2) have suffered from either inadequate sensitivity or extreme instrumental complexity and only very limited results have been reported (4, 5). The purpose of this communication is to report a new technique for SFE analysis, using mass spectrometry, which meets the desired criteria.

## EXPERIMENTAL

The method developed in our laboratory for direct SFE process analysis involves the continuous removal of a small sample for direct mass spectrometric analysis. Recent work in our laboratory (6) has led to the development of a direct fluid introduction (DFI) interface for capillary column supercritical fluid chromatography and mass spectrometry. Similar DFI methods may be used to monitor SFE processes.

Figure 1 gives a schematic illustration of the SFE-MS instrumentation. A Varian Model 8500 high pressure syringe pump is used to maintain the desired pressure in the extraction cell. Extraction cells have been constructed having volumes ranging from 50  $\mu\text{L}$  to 50 mL. The sample to be extracted is placed in the cell and restrained by 1/8" diameter 10  $\mu\text{m}$  filters; an additional 0.5  $\mu\text{m}$  filter is used on the mass spectrometer side of the extraction cell to prevent the passage of particles and possible plugging of the DFI probe orifice. The sample is transported using a 90-cm length of 100  $\mu\text{m}$  i.d. platinum-iridium tubing, through a transfer line, and the DFI probe which is maintained at the same temperature as the extraction cell. For studies at less than 200°C an alternative liquid bath adjacent to the probe is used, reducing the transfer line to 25 cm. The DFI probe terminates with a pressure restrictor having an orifice diameter of approximately 3  $\mu\text{m}$  and a length of 50 to 200  $\mu\text{m}$ . The entire sample line volume is approximately 7  $\mu\text{L}$  and, for our typical flow rates of 5–50  $\mu\text{L}/\text{min}$ , the time from extraction to analysis is less than 1 min. Flow rates as high as 80 to 100  $\mu\text{L}/\text{min}$  can be used (6) if shorter times to analysis are desired. It should be noted that the time delay

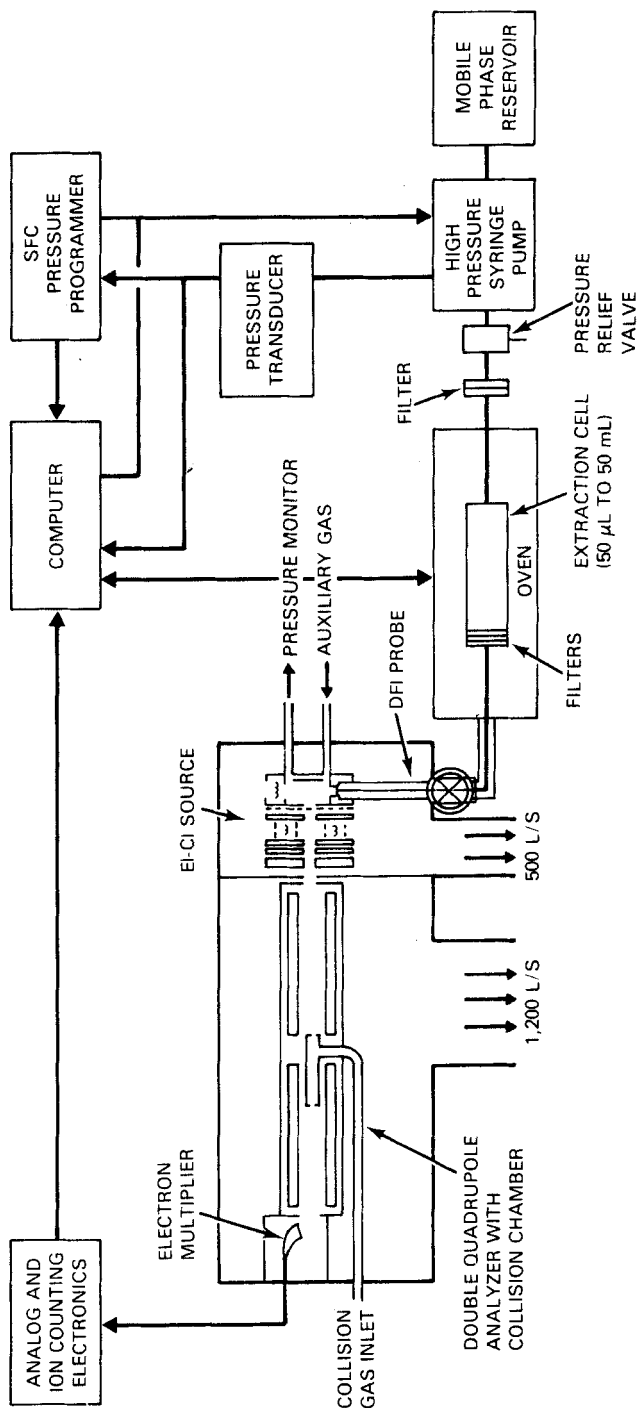


FIG. 1. Schematic illustration of the apparatus for direct analysis of supercritical fluid extraction processes.

does not imply a corresponding time constant in the analysis, and significantly better time resolution can be obtained.

Fluid extracted from the cell is injected directly into the chemical ionization (CI) region of an Extranuclear Laboratories (7) "simultaneous" dual EI-CI source where a constant CI pressure is maintained as described previously (6). The mass spectrometer is an Extranuclear tandem quadrupole mass spectrometer equipped with a cell for collision-induced dissociation (CID) studies (8). The mass spectrometer, pressure regulated pump, oven temperature, and data acquisition have been interfaced for complete computer control.

## RESULTS AND DISCUSSION

The SFE-mass spectrometric apparatus has been successfully demonstrated in our laboratory for a variety of complex samples. The supercritical fluid reaction or extraction processes can be readily studied under both nonisothermal and nonisobaric conditions. Low extraction cell volumes allow evaluation of compounds extracted as a function of pressure for the determination of "threshold pressures" for specific components (2). Large reaction volumes allow one to observe the fluid phase processes as a function of either temperature or pressure where the parameter is varied in some known fashion with time. For large reaction cells ( $>50$  mL) the actual loss due to mass spectrometric sampling ( $<25$   $\mu\text{L}/\text{min}$ ) can be made insignificant for reasonable reaction times. Thus the data obtained in these studies can be made amenable to kinetic analysis using nonisothermal or other deconvolution schemes.

The potential power of the SFE method is illustrated in Fig. 2. A 40-mg sample of a bituminous coal, sized to 80  $\mu\text{m}$  average particle size and previously washed with pentane, was packed into a  $\sim 75$ - $\mu\text{L}$  cell and extracted at  $280^\circ\text{C}$  using a 95% pentane–5% isopropanol mixture. The mass spectra were obtained using the CI mode of operation to reduce most ionic fragmentation. After an initial 2-h period at 10 atm the pressure was increased at a rate of 0.4 atm/min between 10 and 100 atm. There have been many studies of coal extraction using batch autoclave methods (see, for example, Refs. 9–14) but no previous analyses utilizing the capability of direct mass spectrometric sampling. Figure 2 gives normalized reconstructed single ion profiles for eight typical ions as a function of pressure and the total ion current (TIC) profile. The figure illustrates several distinct extraction regions where it is obvious that quite different groups of compounds and molecular weight ranges are being extracted. The variation in the extracted molecular weight distribution with pressure is illustrated in Fig. 3, providing

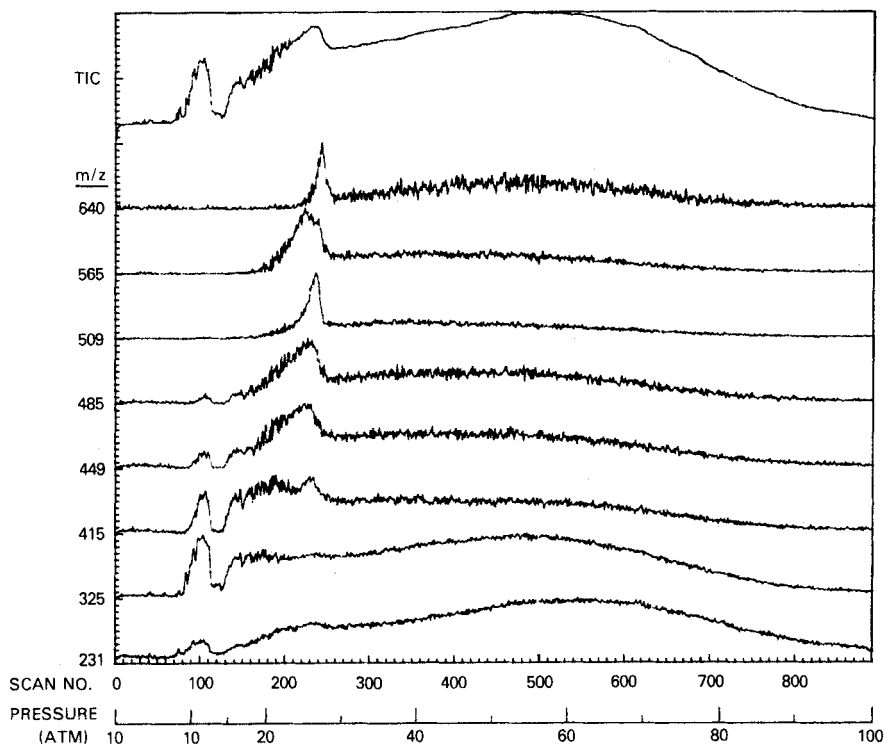


FIG. 2. Total ion current and eight reconstructed selected ion profiles for the direct monitoring of the supercritical fluid extraction of coal in a 95% pentane–5% isopropanol mixture at 280°C. Each profile is normalized to its maximum signal during extraction.

information on chemical nature and molecular weight distribution of the material from the same experiment. Figure 3 gives normalized mass spectra obtained at 10, 12, 20 and 57 atm. More detailed profiles for individual components can, in principle, be obtained by the application of CID methods for materials as complex as coal. Examination of Figs. 2 and 3 shows that large groups of compounds clearly have threshold pressures in the 10–13 and 25–28 atm ranges. Between 40 and 80 atm a large amount of complex higher molecular weight material is extracted shown by the high molecular weight “tail” in the 57-atm spectrum. Examination of the individual mass spectra confirms this observation and demonstrates major shifts in the average molecular weight of the coal extraction products as a function of pressure. Weighing of the coal before and after extraction showed approximately 20% of the coal is extracted under these conditions, in good agreement with previous batch autoclave experiments (11).

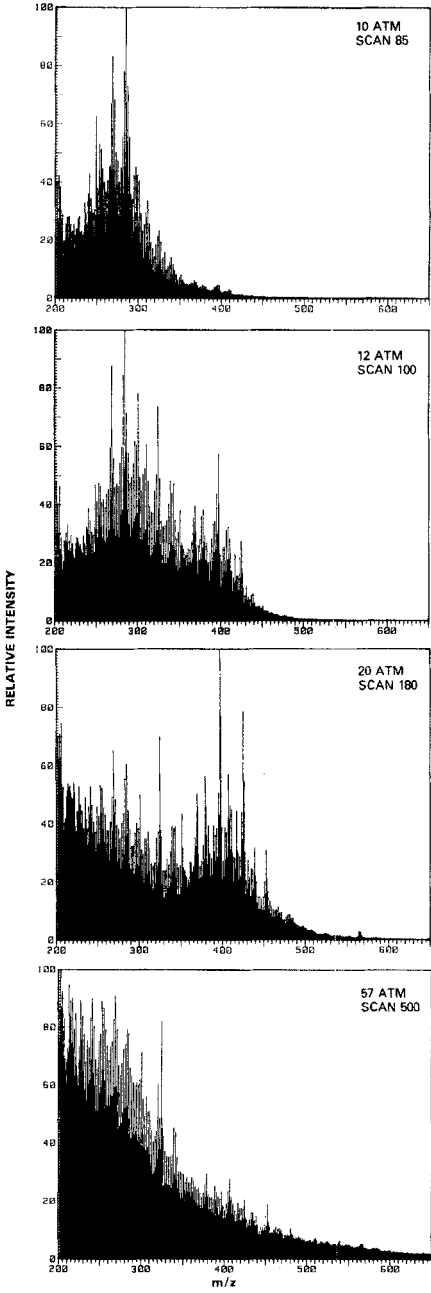


FIG. 3. Mass spectra for four pressures during a supercritical fluid extraction of coal under nonisobaric conditions (see Fig. 2).

These supercritical fluid extraction methods with direct MS analysis have a wide variety of potential applications. These can include the extraction of thermally sensitive or labile compounds using low temperature SF solvents (e.g., CO<sub>2</sub>, ethane) or higher temperature extraction-reaction processes for fuel liquefaction or gasification. Advantages of supercritical fluid extraction methods compared to conventional liquid extraction result from the greater selectivity, since SFE resembles a combination of distillation and extraction (1, 2), and significantly enhanced solubilities for severe conditions or highly compressed gases. Appropriate selection of the solvent system, temperature, and pressure will often allow the highly selective dissolution of a desired product or the removal of a troublesome component. The direct fluid introduction with mass spectrometric detection has been demonstrated to transfer high molecular weight and nonvolatile compounds efficiently to the ionization region (15, 16), extending the range of mass spectrometric application well beyond that possible using conventional gas or direct probe inlet systems. The direct mass spectrometric analysis of these SFE processes on a microscale greatly enhances the practicality of evaluating complex systems to determine optimum extraction parameters.

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## REFERENCES

1. G. M. Schneider, E. Stahl, and G. Wike (eds.), *Extraction with Supercritical Gases*, Verlag Chemie, Deerfield Beach, Florida, 1980.
2. L. G. Randall, *Sep. Sci. Technol.*, **17**, 1-118 (1982).
3. T. H. Gouw and R. E. Jentoft, *Adv. Chromatogr.*, **13**, 1-40 (1975).
4. L. G. Randall and A. L. Wahrhaftig, *Anal. Chem.*, **50**, 1705-1707 (1978).
5. L. G. Randall and A. L. Wahrhaftig, *Rev. Sci. Instrum.*, **52**, 1283-1295 (1981).
6. R. D. Smith, W. D. Felix, J. C. Fjeldsted, and M. L. Lee, *Anal. Chem.*, **54**, 1883-1885 (1982).
7. M. W. Siegel, *Ibid.*, **52**, 1790 (1980).
8. R. A. Yost and C. G. Enke, *J. Am. Chem. Soc.*, **100**, 2274-2275 (1978).
9. K. D. Bartle, T. G. Martin, and D. F. Williams, *Fuel*, **54**, 226-235 (1975).
10. N. Gangoli and G. Thodos, *Ind. Eng. Chem., Prod. Res. Dev.*, **16**, 208-216 (1977).
11. J. Jezko, D. Gray, and J. R. Kershaw, *Fuel Proc. Tech.*, **5**, 229-239 (1982).
12. J. R. Kershaw, *Ibid.*, **5**, 241-246 (1982).
13. J. R. Kershaw and J. Jezko, *Sep. Sci. Technol.*, **17**, 151-166 (1982).



14. K. D. Bartle, D. W. Jones, and H. Pakdel, *Ibid.*, 17, 167-182 (1982).
15. R. D. Smith, J. C. Fjeldsted, and M. L. Lee, Presented at Thirtieth Annual Conference on Mass Spectrometry and Allied Topics, June 6-11, 1982, Paper MOF3.
16. R.D. Smith and H.R. Udseth, *Biomed. Mass Spectrom.*, In Press.

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