

Project Summary

Supercritical Fluid Extraction-Gas Chromatography of Volatile Organic Compounds (VOC) from Tenax Devices

Bob W. Wright, Andrew J. Kopriva, and Richard D. Smith

This report describes the development and evaluation of on-line supercritical fluid extraction-gas chromatography instrumentation and methodology for the analysis of volatile organic compounds (VOC) from adsorbent sampling devices. Supercritical fluid extraction offers potential advantages for the removal and transport of organic components from adsorbent matrices including rapid and efficient extraction at mild temperatures. Extraction at mild temperatures eliminates potential problems such as analyte decomposition that can be encountered with the high temperatures needed for thermal desorption analysis. Since a major objective of this study was to develop viable instrumentation and methodology, a relatively detailed description of the instrumentation design requirements and present limitations are discussed. The results of several series of methodology validation studies are also presented. These studies included recovery studies of standard VOC spiked on three types of Tenax®* sampling devices including authentic actively pumped (volatile organic sampling train, VOST) and passive (EPA) devices (PSD). Replicate devices spiked in an exposure chamber were also subjected to parallel analyses using this new methodology and traditional

thermal desorption gas chromatography.

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

The monitoring of hazardous organic vapors in ambient air is an important concern. A widely utilized approach for these determinations incorporates selective collection and concentration on adsorbent traps followed by either thermal desorption or solvent extraction. For determining volatile organic compounds (VOC), sample collection on Tenax-GC® followed by thermal desorption and gas chromatographic analysis is generally employed. Although some studies suggest that decomposition of analytes and artifact formation can occur during collection, these methods have been widely used and have provided generally satisfactory performance. However, it has become clear as more experience has been gained that serious problems such as analyte decomposition, analyte reactivity, artifact formation, and nonquantitative recoveries can be encountered during the thermal desorption step. These problems can be especially acute for analytes requiring high desorption temperatures (>300°C) and actually limits the volatility range of

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

components that can be successfully desorbed from Tenax®. For instance, 1,1,1-trichloroethane (methyl chloroform) is known to decompose at higher temperatures and undergo dehydrohalogenation during thermal desorption from Tenax®.

Supercritical fluid extraction provides an alternative approach for the removal and transport of organic compounds from adsorbent materials that can be both efficient and thermally mild. 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. The compressibility of supercritical fluids is large and densities typically 10^2 to 10^3 times greater than the gas are obtained. Consequently, molecular interactions increase due to shorter intermolecular distances and solvating characteristics approaching those of the liquid are achieved. However, high diffusion coefficients and low viscosities similar to those of the gas are retained which provide the potential for rapid and efficient extraction rates. By choosing a fluid with a low critical temperature (T_c), such as carbon dioxide ($T_c = 31^\circ\text{C}$), extractions can be carried out at mild temperatures to alleviate any thermally induced problems. Supercritical fluid extraction also provides the potential for removal of less volatile compounds which would require excessively high temperatures for thermal desorption. The combination of on-line supercritical fluid extraction with capillary gas chromatography instrumentally links the extraction and analysis steps and allows the extraction effluent to be directly analyzed. Since this process allows the collection and concentration of trace level analytes at the head of a capillary column, high resolution and high sensitivity analyses can be obtained.

Procedure

Various studies were conducted to expedite the development and initial evaluation of on-line supercritical fluid extraction-gas chromatography (SFE-GC) methodology for the analysis of VOC from adsorbent sampling devices. This was the first investigation conducted to specifically address such an approach for VOC analysis and essentially no previous studies of reports exist relevant to such an analytical approach. This project included the development of appropriate

instrumentation and methodology, evaluation and quantitative validation of the methodology using small sampling devices spiked with standard VOC, and application of the developed methodology to actual passive air sampling devices (PSD) and actively pumped devices (VOST). Tenax® was primarily used as the adsorbent in these studies, but some initial evaluations utilizing Spherocarb® were also conducted.

The on-line supercritical fluid extraction-gas chromatography instrumentation consisted of three primary sections which included a high pressure syringe pump and appropriate extraction cell, an interface region for depressurization of the extraction effluent, and a gas chromatograph with a flame ionization detector. A schematic diagram of the final design of the instrumentation developed in this investigation is shown in Figure 1. The instrumentation was evaluated by analyzing various sampling devices that were spiked with standard VOC mixtures. Devices that had been spiked in an exposure chamber were also subjected to analysis and compared to the results obtained from replicate devices analyzed by traditional thermal desorption gas chromatography.

Results

Supercritical carbon dioxide at temperatures of 50° to 75°C and a pressure of 125 bar provided adequate solvating power to extract the range of VOC utilized in these studies from the Tenax® sampling devices. Relatively clean blank SFE-GC analyses could be obtained from Tenax® sampling devices, but high levels of contamination from Spherocarb® sampling devices persisted even after prolonged conditioning with supercritical fluid extraction. Consequently, only Tenax® sampling devices were subjected to detailed evaluation.

Quantitative extraction of the analytes from the sampling devices required several fluid volumes of the device to be used. Thus, large volumes of gas from the depressurized carbon dioxide (several liters) were required to be passed through the chromatographic column. This requirement imposed the following specific instrumental constraints:

1. Minimum dead-volume construction of the sampling device extraction cells was required to minimize extraction fluid volumes.
2. Ultrapure carbon dioxide was necessary to prevent concentration of impurities.

3. A wide-bore (0.53 mm i.d.) chromatographic column was needed to provide maximum gas flow and to maintain high chromatographic separation efficiency for the sampling devices examined in this work.

The large gas volume and high flow rate impaired efficient analyte concentration which required extreme focusing methods of whole column cryotrapping at -50°C with a thick-film (5 μm) stationary phase and a 15 m long retention gap.

Good quantitative agreement between the spike and recovery levels of the VOC were obtained for the smaller volume adsorbent devices. The larger volume sampling devices (e.g., actively pumped) presented greater challenges and required extraction times in excess of 30 minutes to obtain complete removal of the analytes. Longer extraction times impaired efficient chromatographic separations and less reliable quantitative recovery levels (and greater departure from the spike levels) were obtained. The broadened peaks from less efficient separations generally corresponded to greater than quantitative recoveries. The quantitative SFE-GC analyses of the PSD and VOST devices spiked in the exposure chamber were ambiguous due to poorly resolved compounds and coeluting contaminants that were extracted from the Tenax® matrix. However, peaks matching the appropriate retention times of the spiked VOC could be distinguished. Preliminary investigations utilizing various PCB (polychlorinated biphenyl) congeners suggested that extension of the SFE-GC methodology to the analysis of semi-volatile materials from Tenax® sampling devices would also be feasible.

Conclusions and Recommendations

The general concept of combined on-line supercritical fluid extraction-gas chromatography proved viable for the quantitative extraction, recovery, concentration, and analysis of standard volatile organic compounds that were spiked on Tenax® sampling devices. No apparent physical changes or deleterious effects on the sorption behavior of the Tenax® were observed after numerous (>20) supercritical fluid extraction cycles. However, some minor caking of the adsorbent was observed after extensive exposure and supercritical fluid extraction cycles.

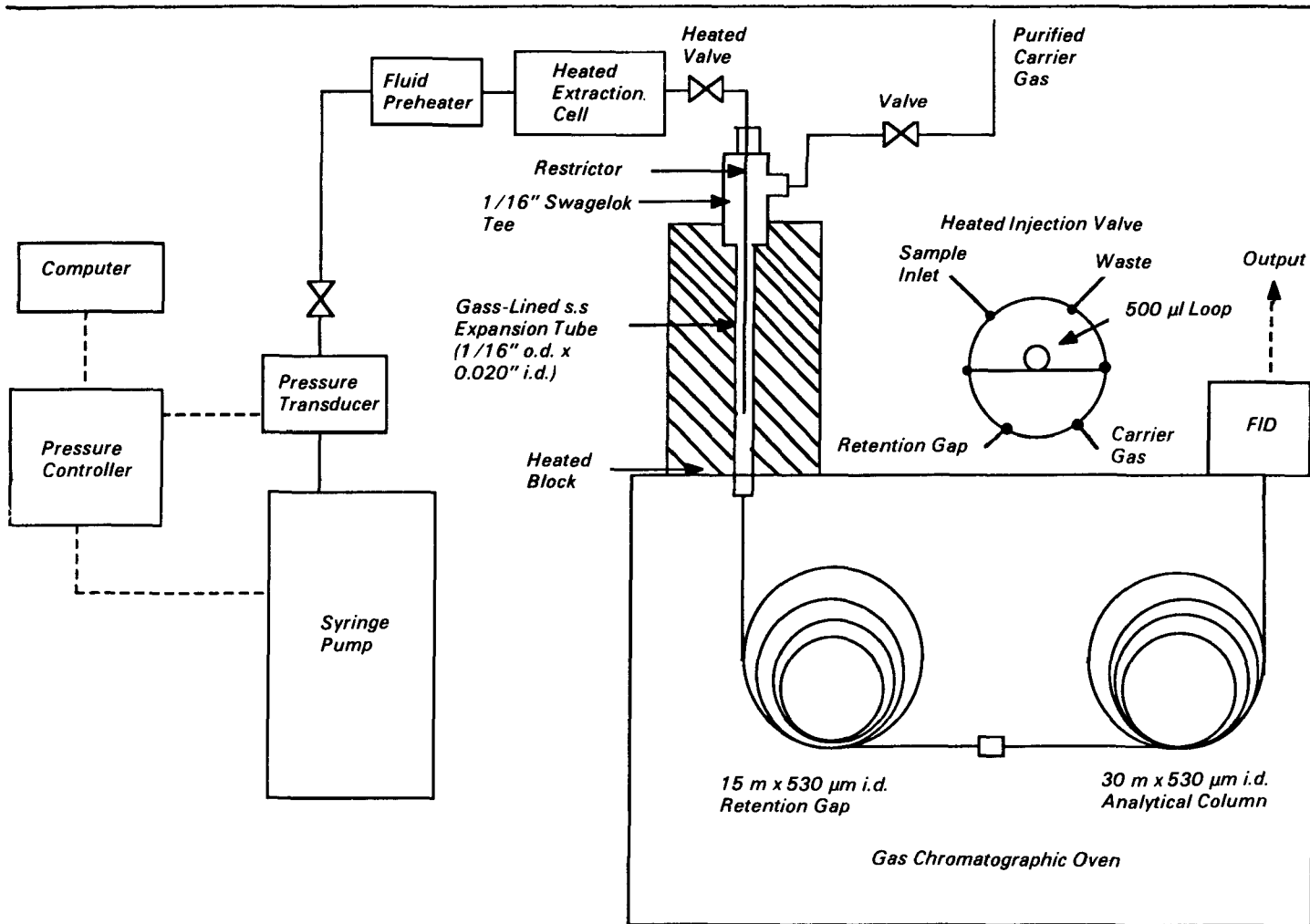


Figure 1. Schematic diagram of the final design of the on-line SFE-GC instrumentation.

A number of recommendations for additional studies can be made. Improved analyte trapping methods need to be developed to increase the separation efficiency for the more volatile compounds and to allow faster extraction rates without compromising the chromatographic separation quality. This could be done by using longer analytical columns, longer retention gaps (e.g., 50 m) and/or incorporation of an integral baffle zone consisting of a short length of column packed with particles of deactivated Chromosorb W® or glass beads. Smaller sampling devices would also improve overall performance, but the impact upon detection limits would require study. With the development of improved trapping methods, faster extraction rates should be developed and the limitations on analysis speed defined. For smaller volume devices, extraction times of five minutes or less should be

conceivable. Sampling devices optimized for the SFE-GC methodology should also be designed and evaluated.

Additional quantitative studies should be done using rigorously prepared standard mixtures for adsorbent exposure and instrument calibration. Improved quantitative reliability could also be obtained by utilization of a mass selection detector (MSD) to eliminate potential interferences from coeluting contaminants. These studies should also include standard VOC that present problems for thermal desorption analyses.

The extraction cells for the sampling devices should be redesigned to use stainless steel O-rings rather than the present polymer O-rings to eliminate the possibility of organic contaminants being leached from the O-rings.

A rigorous investigation for the extension of SFE-GC methodology to the analysis of semi-volatile materials from

adsorbent sampling devices should be conducted and the range of compounds that could be analyzed from a single analysis defined (including detection utilizing an MSD). In addition to Tenax®, such a study could include the evaluation of other adsorbent materials. For instance, Sphero carb®, or another carbon molecular sieve material that was properly purified (perhaps using supercritical fluid extraction with a highly solvating fluid) could be utilized.

A related study on the effects of supercritical fluid extraction on the sorbent properties of the utilized adsorbents (e.g., Tenax® and perhaps Sphero carb®) should be conducted. Such a study would include rigorous evaluation of the retention volumes of selected standard VOC on adsorbents exposed to various supercritical fluid extraction conditions (e.g., fluids, densities, exposure times).

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

The complete report, entitled "Supercritical Fluid Extraction-Gas Chromatography of Volatile Organic Compounds (VOC) from Tenax Devices," (Order No. PB 88-124 300/AS; Cost: \$14.95; subject to change) will be available only from:

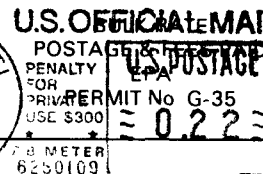
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