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SORBENT-BASED METHOD FOR THE ANALYSIS OF AMBIENT AIR USING SUPERCRITICAL FLUID DESORPTION/GAS CHROMATOGRAPHY

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The work described in this paper shows how we have investigated the utility of polar polyimide sorbents for the collection of polar and non-polar volatile organic compounds in ambient air. The results indicate that supercritical carbon dioxide can be used to recover a variety of compounds with a wide range of volatilities from polyimide sorbents and that these compounds can be effectively collected onto an adsorbent micro-trap after the expansion of the fluid prior to thermal desorption gas chromatographic analysis. Molecular sieve 3A was used and found to have a very high capacity for removal of water from the supercritical fluid extract stream. The sieve tended to adsorb polar compounds in the absence of water; the presence of water sometimes reduced analyte adsorption. The method was used to collect, recover, and analyze volatile organic compounds from the air of a laboratory building and was shown to be quite sensitive for appropriate compounds.

KEY WORDS: Supercritical Fluid Extraction (SFE), SFE/Gas Chromatography (SFE/GC), thermal desorption, environmental air analysis, polyimide sorbents.

INTRODUCTION

Sorbent-based Sampling

As the level of understanding about the effects on human health of chronic exposure to low levels of toxic organic compounds improves, it has become increasingly clear that the analytical chemist must be able to sample and analyze these compounds in air, both in occupational and environmental settings, at ever-lower levels. This presents a formidable challenge not only because of the wide distributions of both molecular weight and polarity of the compounds, but also because of the trace levels at which these compounds are often present. One of the most useful methods to overcome the problem of low analyte concentration is to use a sorbent such as Tenax-GC.^{1,2} In such an analysis, an air stream is drawn through a cartridge packed with the sorbent material and the organic compounds are selectively retained. The trapped compounds are subsequently thermally desorbed and cryogenically focused onto the head of a gas chromatographic column for analysis. Mass spectrometric detection (GC/MS) is often used to obtain qualitative and quantitative information.

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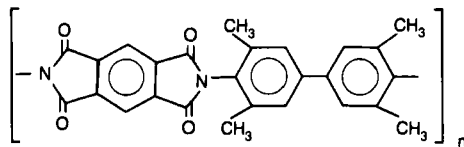


Figure 1 Polyimide 109.

Despite the power and advantages of these preconcentration techniques, there are some limitations to their applicability. One such limitation, which can also be considered an advantage, depending on the goal, is the selectivity of the sorbent towards toxic chemicals of different polarities. Tenax-GC, for example, retains nonpolar compounds much more efficiently than polar compounds such as methanol giving Tenax-GC a clear advantage for nonpolar chemical analysis.² This selectivity results in "breakthrough" of the polar compounds while the nonpolar materials are still being effectively concentrated and the inability to quantify such poorly retained, polar chemicals. If smaller volumes of air are sampled such that polar compounds do not breakthrough, the resulting method limit of detection can be inadequate. It is therefore extremely important that the analysts utilize a thorough understanding of the sampling goals and method limitations so that adequate sensitivity is obtained and the resulting quantification is valid.

An increase in the polarity of the sorbent should result in an increase in the breakthrough volume of polar compounds and potentially provide for a more widely applicable method for these types of chemicals. This was the premise of the previous preparation of many polyimide-based sorbents.³ Of the many polymers synthesized, several of the materials displayed good retention of polar compounds, good thermal stability (necessary for use with thermal desorption methods), and low background. Four of these polymers were selected for more detailed characterization and the sorbent demonstrating the greatest retentive nature (Polyimide 109 (PI-109) Figure 1) was used in the current work.^{4,5}

Removal of Adsorbed Water Vapor

Although the increased polarity of the sampling medium provides for improved retention of polar organic compounds, it also results in the collection of substantial amounts of water during the sampling process since water is present in the atmosphere at levels much higher than the compounds of interest. This water creates a variety of problems in the analytical step (GC/MS) including closure of the cryogenic trap during thermal desorption and substantial pressure increases in the mass spectrometric detector during elution of the water vapor from the gas chromatographic column. For methods not involving MS detection, cryogenic interfaces can be designed such that closure of the trap does not occur. However, we have observed irreproducible shifts in GC retention times as large amounts of

water vapor elute over several minutes. This would interfere with the identification and quantitation of analytes in and near the water elution region. It is apparent, then, that any method making use of a polar sorbent must have provisions for the removal of water prior to the analytical step.

Many techniques for the removal of water from a gas stream containing organic compounds, i.e., during sample collection, have been reported in the literature. Among these are the use of K_2CO_3 , $Mg(ClO_4)_2$, and 5A and 3A Molecular Sieves,^{6,21} 4A Molecular Sieve, $CaSO_4$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, and K_2CO_3 ,⁷ $CaSO_4$, Na_2SO_4 , and 5A Molecular Sieve,⁸ and semi-permeable Nafion membranes.^{9,10} Nafion dryers have been shown to be satisfactory for non-polar compounds⁹ yet greatly reduce the recoveries of polar compounds such as 2-nonanone, 1-nonanol, acetone, and ethyl acetate.¹⁰ Of the desiccants which rely on a chemical reaction, K_2CO_3 provided the best recoveries of both polar and nonpolar compounds and indicate that molecular sieves, which utilize size-dependent adsorption, can retain polar, oxygenated compounds.^{6,7} Another study found that 5A Molecular sieve provided very good recoveries for acetone, butyl acetate, and methyl isobutyl ketone at the ppm level and suggested that this apparent contradiction was the result of using only 220 mg of the sieve to dry the air stream as compared to the much larger masses used by the earlier researchers.⁸ In addition, the study showed that the molecular sieve had the largest capacity for the adsorption of water. The method we envisioned would make use of a drying step integrated into the analytical (GC) portion of the method so that sampling in the field would not be encumbered by the need for a drying cartridge before each sorbent cartridge. In addition, we wanted to be able to regenerate the desiccant between each analysis through a simple thermal treatment. Given these considerations, we chose to test molecular sieves as potential desiccants.

Supercritical Fluid Extraction

One concern which remained, however, was the evidence for adsorption of polar compounds on molecular sieves under some conditions.^{6,7} Because these studies utilized drying in the vapor phase, we felt that some improvement could be found in using the material to remove water from a supercritical carbon dioxide stream containing the desorbed chemicals. Under these conditions, the fluid would have a greater ability to solvate the organic compounds than would a gas, and that this might result in uniformly high recoveries for both nonpolar and polar compounds. The use of supercritical CO_2 for desorption of trapped chemicals might also extend the range of applicability of sorbent-based sampling methods to those compounds not amenable to thermal desorption, including both compounds of limited volatility as well as those which are thermally labile. This has been suggested and shown to be feasible in studies which demonstrated the ability of supercritical CO_2 to recover organic compounds from XAD-2 resin, polyurethane foam (PUF), Spherocarb, and urban dust,^{11,12} as well as organic compounds from polyimide sorbents and from Tenax-GC.^{5,13}

Many researchers have used supercritical fluid extraction (SFE) in conjunction with a chromatographic system to provide for methods which require minimal

sample preparation. SFE coupled directly with gas chromatography (SFE/GC) has been used in the analysis of polynuclear aromatic compounds (PAH) from urban dust, coal tar and river sediment,^{14,15} phenolic compounds from wood smoke particulates,¹⁵ and flavor and fragrance compounds from natural products.¹⁶ SFE has also been coupled with supercritical fluid chromatography (SFE/SFC) for the analysis of sulfonyl urea herbicides and their metabolites from soil, plant materials, and a cell culture medium.¹⁷ The SFE/GC interface typically involves the expansion of the supercritical fluid extract into a retention gap in-line with a capillary GC column or into the column itself; the gap or column is often cooled to allow more efficient focusing of more volatile compounds. However, compounds with relatively high volatilities ($<C_8$) often remain poorly focused and results in poor chromatography.¹⁶ Because we wished to study the utility of SFE/GC for the analysis of volatile organic compounds of environmental interest, we chose to refocus the extracted compounds onto a second, smaller sorbent trap prior to thermal desorption/GC.

The overall goal of the current work is to improve the ability to sample and analyze toxic, polar organic compounds in air. Towards this end, methods for the removal of high levels of co-adsorbed water must be investigated and the entire collection, extraction and chromatographic procedure studied using model compounds containing a wide range of chemical functionalities.

EXPERIMENTAL

Drying of the Supercritical CO₂ Stream

The importance of removing water adsorbed to the polymeric sorbent during sample collection prior to chromatographic analysis was discussed above. The capacities of 3A molecular sieve (14–30 mesh, W. R. Grace) and an aluminum phosphate-based molecular sieve (AlPO-5, synthesized at Research Triangle Institute) were investigated for this purpose. The material of interest was packed into a 6.3 mm (0.25 inch) o.d. by 4.5 mm i.d. stainless steel tube with 2 μ m fritted end-fittings and having a volume of 0.8 mL. The resulting masses of desiccants were 700 mg in each case. This cartridge was placed into an oven held at 40 °C and the inlet connected, through a Rheodyne injection valve, to a Brownlee Labs (Applied Biosystems) dual syringe micro pump which provided the high pressure CO₂ (Linde, bone dry grade). The CO₂ was passed through an activated alumina trap prior to loading into the pump. The outlet was connected through an on/off valve to a 30 cm length of 25 μ m i.d. fused silica tubing which provided the back-pressure necessary to maintain supercritical fluid conditions. The outlet of the fused silica tubing was placed into a heated 1.6 mm (1/16 inch) stainless steel sleeve which directed the effluent into a 0.25 mm (0.01 inch) i.d., 1.6 mm (1/16 inch) o.d. coiled tube held at -68 °C. Incremental injections of water were made into the 20670 kPa (3000 psi) CO₂ stream while the flow at the outlet of the cooled tube was monitored. The flow rate at the exit dropped from approximately 150 mL/min

to 0–5 mL/min when the capacity of the test material was exceeded and water froze in the coiled tube. Experiments performed in the absence of molecular sieve indicated that 4–5 μ L of injected water was sufficient to plug the cooled tube and thus served as our “zero value”. The capacity of the material was calculated as the mass ratio of water to sieve, corrected for the zero value. The cartridges were regenerated between experiments by heating to 260 °C with 8 mL/min helium flow for 45–60 minutes.

The absorptive nature of each drying agent was investigated by determining the recoveries of gamma-[$^{14}\text{C}(\text{U})$]BHC (1,2,3,4,5,6-hexachlorocyclohexane), which is also referred to as BHC, [$9\text{-}^{14}\text{C}$]anthracene, [ring-2,6- ^{14}C]Parathion (Amersham Corp., Arlington Heights, IL) and [$^{14}\text{C}(\text{U})$]-2,3,5,2',3',5'-hexachlorobiphenyl (PCB, Pathfinder Labs, St. Louis, MO) from Tenax-GC through the desiccant cartridge as in the method previously reported.¹³ Desorption gas volumes up to 5 L were used for these recovery experiments.

Supercritical Fluid Extraction and Transfer to the GC Column

The test compounds used in the current work were ethanol, acrolein, acetone, acrylonitrile, dichloromethane, *n*-hexane, ethyl acetate, 1,2-dichloroethane, benzene, pyridine, *n*-propylbenzene, phenol, benzonitrile, and 1,2-dichlorobenzene. These compounds were chosen based on the concern over occupational and environmental exposure, the wide range of functional groups represented (much like the McReynold's test compounds), and the ability of the gas chromatographic column to completely resolve the components in the test mixture. These compounds were combined in such a way that 1 μ L injected into a split GC injector would load approximately 1 μ g of each component onto the polyimide sorbent cartridge. No solvent was used. After injection, 8 mL of helium carrier swept the components onto the sorbent bed (4 min at 2 mL/min). The effect of water vapor on the extraction and recovery process was tested by loading the compounds onto a sorbent cartridge previously equilibrated with water vapor. This was accomplished by purging the cartridge overnight with approximately 15 L helium saturated with water at room temperature.

The extraction and recollection device used is diagrammed in Figure 2. Test compounds were loaded onto the adsorbent cartridge (sorbent trap) consisting of a 6.3 mm (0.25 inch) o.d. \times 5.3 mm i.d. \times 10 cm stainless steel tube, fritted (2 μ m) column end fittings and packed with approximately 400 mg of 40–60 mesh Polyimide 109. The loaded cartridge was then assembled into the device of Figure 2 such that the adsorbed compounds would be desorbed in the reverse direction from that of loading. The oven temperature was brought to 40 °C and, with valve 2 closed, the CO₂ pressure was raised to 10 335 or 20 670 kPa (1500 or 3000 psi) corresponding to densities of 0.65 and 0.84 g/cc respectively. After checking for leaks, valve 2 was opened and the extraction was begun. The supercritical effluent was expanded through a length of 25 μ m i.d. fused silica tubing into a heated stainless steel sleeve which directed the gas stream onto a micro-trap held at –45 °C in a liquid/solid acetonitrile bath. This temperature was needed to maintain the CO₂ in its gaseous state; lower temperatures resulted in liquefaction.

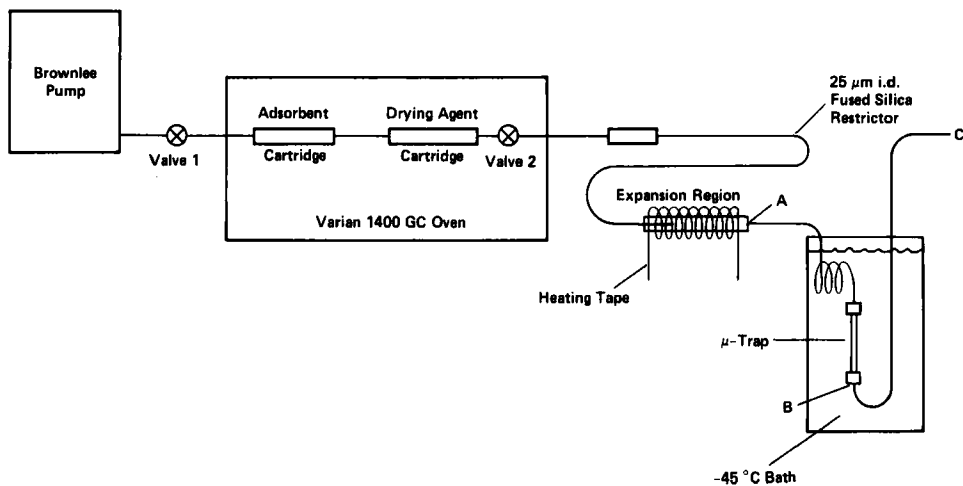


Figure 2 Supercritical Fluid Extraction/Recollection Apparatus. A, B, and C as defined in the text.

The micro-trap served to selectively adsorb the organics from the dry CO_2 stream and consisted of a 1/16 inch o.d. \times 0.04 inch i.d. \times 6 cm or 12 cm nickel tube packed with 120–140 mesh polyimide 109; the mass of polymer was 7 and 14 mg for the 6 and 12 cm micro-traps, respectively. Extraction was allowed to proceed until a gas volume of 1 L was measured at C (Figure 2); the time involved was typically about 10 minutes. At 10 335 kPa (1500 psi), 1 L of gas corresponds to 3 mL of supercritical fluid and at 20 670 kPa (3000 psi), 1 L of gas corresponds to 2.3 mL of fluid.

After the extraction was complete, the CO_2 flow was stopped by closing valve 2. The connection at A (Figure 2) was immediately broken and sealed with a stainless steel fitting. The outlet at C was closed with a cylindrical septum and the trap was removed from the cold bath and allowed to warm to room temperature. Any liquid acetonitrile adhering to the outside of the trap was removed with a disposable absorbent tissue. The connection at B was broken and immediately connected to the inlet of a 60 m \times 313 μm i.d. DB-5 gas chromatographic column with a 1 μm film thickness (J&W Scientific) installed in a Varian 3700 Gas Chromatograph. The fitting at A was connected to the carrier gas (He) line and the first part of the column was cooled to -196°C with liquid nitrogen before flow was begun. The system was quickly checked for leaks, the micro-trap was placed into a heating block held at 260°C , and thermally desorbed for 25 minutes at the column flow rate of 2 mL/min. After this time, the liquid nitrogen Dewar was removed and the temperature of the column was held at 20°C for four minutes then programmed to 200° at 3° per minute. The signal from the flame ionization detector was integrated using a Hewlett Packard 3390A integrator. Prior to re-use, the large sorbent trap and sieve cartridge were extracted with approximately 15 mL of supercritical CO_2 (40°). In addition, the sieve cartridge was thermally desorbed for 45 minutes at 220° and a helium flow of 30 mL/min.

Storage Experiments

Sorbent cartridges are often stored for some time prior to analysis. During this

time, adsorbed analytes can diffuse into the sorbent which can lead to poor recoveries. In order to test this for PI-109, we loaded four cartridges with the test compounds after the equilibration of the sorbent with water vapor as described above. Immediately after loading, the cartridges were capped using compression fittings, and placed into glass culture tubes that were then placed into a clean paint can that was then sealed and stored in the refrigerator. Two of the samples were desorbed and analyzed, as described above, after one week and the other two were desorbed and analyzed after three weeks.

Air Sampling Application

A preliminary, qualitative test of the method was accomplished by sampling the atmosphere in the lobby of a laboratory building during the routine application of pest control substances and in a synthetic organic chemistry laboratory at RTI. Samples were taken by connecting the PI-109 sorbent cartridge to a Thomas double diaphragm pump and drawing air through the sorbent bed at a flow of approximately 17 mL/min. The flow through each cartridge was measured with a calibrated rotameter at the beginning and end of the 6–7 hour sampling period. In each setting, a charcoal tube-based air sample was collected, desorbed with carbon disulfide, and analyzed by GC to allow a qualitative comparison.

RESULTS AND DISCUSSION

Removal of Water from Supercritical CO₂ Stream

The capacity of the 3A molecular sieve for water is stated to be 10% (weight:weight) in a gas and 4–6 weight % in a liquid.¹⁸ Because a supercritical fluid has physical properties (diffusivity, density) intermediate between those of a gas and a liquid, it seemed reasonable to expect that the capacity for water in a supercritical fluid might be intermediate in value. This turned out not to be true. The results indicate that the water capacity of the 3A molecular sieve in a CO₂ stream at 3000 psi and 40 °C is approximately 60 weight %. This surprisingly high capacity is presumably a manifestation of the higher pressure forcing water deep into the molecular sieve structure. Under the same conditions, the capacity of the AIPO-5 dessicant was found to be 40 weight %.

Given the good water capacities of each of the potential desiccants, the choice of which to evaluate further would be based on the observed adsorptive behaviors. The recoveries of the radiolabelled test compounds through each material are shown in Table 1. The recoveries of BHC and hexachlorobiphenyl through each material were essentially the same. Anthracene was marginally recovered from the molecular sieve and not all from the AIPO-5. The more polar parathion was not recovered from either material. Although there were recovery problems with these compounds, the extent and selectivity of the adsorption of a variety of polar compounds was not clear. We chose to characterize the performance of the

Table 1 Recovery of radiolabelled test compounds through desiccant materials

Compound	% Recovery ^a	
	3A Sieve	AIPO-5
BHC	80	76
PCB	77	73
Anthracene	64	— ^b
Parathion	— ^b	— ^b

^a% Relative standard error estimate $\leq 10\%$ in all cases. All analyses performed in duplicate.

^bElution of compound through a desiccant bed was not observed at 3000 psi and 40°C. Actual recoveries were not determined.

“better” desiccant, 3A molecular sieve, to dry a supercritical fluid stream containing polar, volatile analytes.

SFE/GC

One of our first concerns was the behavior of the supercritical fluid desorption/micro-trap/thermal desorption GC system in the absence of any loaded compounds. The system blank is shown in Figure 3A. The large peak at the beginning (system peak), was routinely observed and presumably arises from impurities in the CO₂ or through the use of SFE grade CO₂ (Scott Specialty Gases), recently introduced, this peak could be minimized. This is consistent with earlier SFE/GC work¹⁹ and that compounds loaded directly onto the micro-trap with helium and thermally desorbed onto the GC column showed no such peak. With some additional purification of the CO₂, or through the use of SFE grade CO₂, (Scott Specialty Gases), recently introduced, this peak could be minimized. The gas chromatogram resulting from test compounds taken through the procedure in the absence of a drying step is shown in Figure 3B. Replicate analyses revealed consistently good recoveries for all of the test compounds except dichloromethane and *n*-hexane which break through the micro-trap, presumably a result of discrimination by the polar PI-109 combined with their volatility. We also discovered that some of the measured recoveries as determined through area count comparisons to response from direct syringe injection were higher than expected, e.g., phenol, which indicated a lack of proper calibration for the loading of the large sorbent cartridge. By normalizing the responses of the test compounds to that of benzene for each analysis, consistent relative recoveries were obtained for each compound. Although this made a rigorous quantitative study impossible, much useful information about the qualitative behavior of this new analytical approach to air analysis for polar molecules was obtained.

The effect on the recoveries as a result of a drying step is shown in Table 2. The numbers presented represent the ratios of the normalized recoveries with a drying step to the normalized recoveries in the absence of a drying step; a value of “1” would represent an unchanged recovery. The most revealing information is found

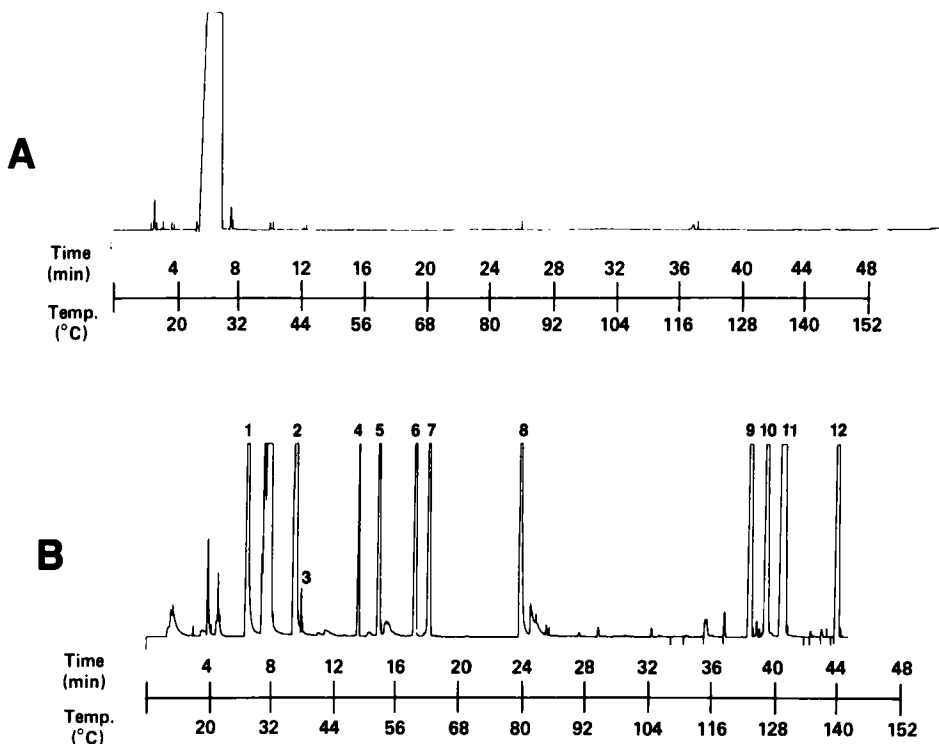


Figure 3 Comparison of system blank (A) and standard compound (B) analysis in the absence of a drying step. Note that the carrier flow rates were not identical. Peak identification as follows: 1 = ethanol, 2 = acrylonitrile, 3 = dichloromethane, 4 = *n*-hexane, 5 = ethyl acetate, 6 = 1,2-dichloroethane, 7 = benzene, 8 = pyridine, 9 = *n*-propylbenzene, 10 = phenol, 11 = benzonitrile, 12 = 1,2-dichlorobenzene. In this analysis (B), acrolein and acetone eluted with the system peak.

in the greatly reduced recoveries of acrylonitrile, ethyl acetate, pyridine, phenol and benzonitrile, all of which are polar compounds. The relative recoveries of the nonpolar compounds dichloroethane, *n*-propylbenzene and 1,2-dichlorobenzene remained good. Tripling the extraction volume improved the recoveries of the nonpolar compounds yet did little to improve those of the polar compounds. A second 3 L extraction of the sorbent cartridge recovered additional amounts of acrylonitrile, ethyl acetate, and benzonitrile (65%, 77%, and 86% more respectively). Clearly, polar analytes were interacting very strongly with the desiccant material. Also, because the pore size of the sieve is such that the compounds themselves are excluded from the pores, these interactions are occurring on the surface of the sieve particles.

The use of a higher extraction pressure, and the concomitant increase in fluid density, might favor a greater solvation of the analytes by the mobile phase and result in improved recoveries of the polar compounds. The results of extraction at 20 670 kPa (12 cm micro-trap) are shown in column 3 (20 670 kPa, dry) of Table 3. The higher fluid density provided good recoveries for the nonpolar compounds yet

Table 2 Effect of drying step (3A molecular sieve) on test compound recoveries at 10 335 kPa and 40 °C

Compound	Ratio (1 L gas volume) ^a	Ratio (3 L gas volume) ^a
Polar compounds		
Ethanol	— ^{b, c}	— ^b
Acrolein	— ^{b, c}	— ^b
Acetone	— ^b	— ^b
Acrylonitrile	0.11 (0.09) ^c	0.26 (0.3) ^{c, e}
Ethyl acetate	0.05 (0.05) ^c	0.10 (0.04) ^{c, e}
Pyridine	0.003 (0.001) ^c	0 ^c
Phenol	0 ^c	0 ^c
Benzonitrile	0.07 (0.07) ^c	0.29 (0.17) ^{c, e}
Nonpolar compounds		
Dichloromethane	— ^d	— ^d
<i>n</i> -Hexane	— ^d	— ^d
1,2-Dichloroethane	0.90 (0.17)	0.96 (0.33)
Benzene	1.0 (—)	0.98 (0.39)
<i>n</i> -Propylbenzene	0.83 (0.14)	0.96 (0.11)
1,2-Dichlorobenzene	0.74 (0.15)	0.98 (0.06)

^aThe ratio is as defined in the text. Except for extraction volume, all parameters were held constant. For the 3 L extractions absolute recovery ratios were used because the larger volume caused large losses of benzene from breakthrough. Analyses were performed in duplicate and the standard error estimate S_e is given in parentheses.

^bAnalyte peak was unresolved from the system impurity peak in either test (with sieve) or control (no sieve) analyses.

^cThese compounds were recovered in excess of 85% in the absence of the drying step.

^dDichloromethane and hexane broke through the micro-trap; a ratio here would have little meaning.

^eSignificant quantities of these compounds (65–86% more) were recovered by a second 3 L extraction (see text).

did little to improve the recoveries of the polars. Note that the use of the longer micro-trap provided improved recovery of dichloromethane indicating that earlier poor recoveries for the compound were indeed due to premature breakthrough.

The extraction of the test compounds from a dry sorbent bed, i.e., compounds loaded onto a dry sorbent with dry helium carrier, represents an artificial situation because any real air sampling will usually take place in an atmosphere with greater than 0% relative humidity. Because it is known that the presence of water can greatly affect the retention of compounds on polar polyimide sorbents,⁴ it is not unreasonable to expect that water dissolved in a supercritical fluid stream, as a consequence of extracting a "wet" sorbent, might affect the retention of polar compounds on the 3A molecular sieve. This was tested by extracting the test compounds from a sorbent cartridge equilibrated with water vapor prior to loading. The results of these experiments are shown in Table 3. No improvement was seen for any of the polar compounds with the exception of phenol, the relative recovery of which improved from 0 to 0.14 at 10 335 kPa (1500 psi) and 0.43 at 20 670 kPa (3000 psi). Such a change suggests that the level of water can affect not only sampling but also the desorption process and that the behavior of the system under a variety of conditions needs to be well characterized.

Given the good capacity of the molecular sieve for water under supercritical fluid conditions, the mass of sieve in the cartridge was reduced by 39% (4.9 cm length reduced to 3.0 cm length) and the recoveries of the test compounds extracted from wet sorbent were determined. Conditions were 20 670 kPa (3000 psi)

Table 3 Relative recoveries of test compounds through 3A molecular sieve using different extraction conditions

Compound	Extraction condition ^a		
	10 335 kPa, wet ^b	20 670 kPa, dry ^b	20 670 kPa, wet ^b
Polar compounds			
Ethanol	N.D. ^c	— ^d	— ^d
Acrolein	N.D.	— ^d	— ^d
Acetone	0.2 (0.11)	— ^d	— ^d
Acrylonitrile	0.05 (0.053)	0.18 (<i>n</i> = 1)	— ^d
Ethyl acetate	0.02 (0.022)	0.15 (<i>n</i> = 1)	0.02 (0.03)
Pyridine	N.D.	0.006 (0.008)	N.D.
Phenol	0.14 (0.07)	N.D.	0.43 (0.10)
Benzonitrile	0.03 (0.02)	0.11 (0.10)	0.06 (0.08)
Nonpolar compounds			
Dichloromethane ^e	0.58 (0.01)	0.59 (<i>n</i> = 1)	1.05 (0.08)
<i>n</i> -Hexane ^e	0.07 (0.01)	0.07 (<i>n</i> = 1)	0.18 (0.07)
1,2-Dichloroethane	1.01 (0.03)	1.03 (0.29)	0.95 (0.10)
Benzene	1.0 (—)	1.0 (—)	1.0 (—)
<i>n</i> -Propylbenzene	0.90 (0.13)	1.13 (0.28)	0.87 (0.10)
1,2-Dichlorobenzene	0.86 (0.14)	1.06 (0.25)	0.86 (0.09)

^aAll extractions were carried out at 40°C using the 12 cm μ -trap and 1 L CO₂ gas volume.

^bRecoveries are expressed relative to benzene. *S_x* is given in parenthesis. The first two columns were analyses performed in duplicate. The extractions at 20 670 kPa from wet sorbent were performed in triplicate.

^cN.D. = not detected.

^dCompounds were unresolved from the system peak.

^e*n*-Hexane consistently broke through the μ -trap. Dichloromethane recoveries were very sensitive to small extraction volume differences. Little importance should be placed on these recovery values.

Table 4 Relative recoveries of compounds desorbed from stored cartridges

Compound	1 Week recovery Control recovery (<i>S_x</i>)	3 Week recovery Control recovery (<i>S_x</i>)
1,2-Dichloroethane	0.85 (0.07)	0.60 (0.05)
Benzene	0.70 (0.08)	0.68 (0.07)
<i>n</i> -Propylbenzene	0.74 (0.02)	0.58 (0.02)
1,2-Dichlorobenzene	0.71 (0.03)	0.60 (0.08)

Compounds were recovered by extracting the compounds from wet sorbent, through the 4.9 cm 3A sieve cartridge. Conditions: 40°C, 10 335 kPa (1500 psi), 1 L gas volume and 12 cm micro-trap. Analyses were performed in duplicate.

and 1 L CO₂ gas volume as in Table 3. It was hoped that the smaller mass of molecular sieve would result in improved recoveries for the extracted test compounds; such significant improvements in the recoveries were not noted.

All of the results obtained to this point were from sorbents loaded and then analyzed immediately. In a real sampling situation, the cartridges might need to be stored for a time prior to analysis. The results of the storage experiments are shown in Table 4 for the well-retained nonpolar analytes. Both the polar and nonpolar test compounds were used. However, because the sorbent was pre-equilibrated with water the 3A molecular sieve cartridge was used during desorption. As a result, the polar compounds were not recovered because the

Table 5 Sampling and analysis of laboratory air for organic compounds

<i>Compound^a</i>	<i>Area counts of peaks from SFE/GC analysis</i>	<i>Approximate conc. (ppm)^b</i>	<i>Found in charcoal sample</i>
Chloroform	641 585	0.11	✓
Dichloromethane	1 626 750	0.39	✓
<i>n</i> -Hexane	2 084 000	0.07	✓
Carbon tetrachloride	994 220	0.13	✓

^aIdentity based on GC retention compared to standard compounds.

^bFor illustrative purposes only.

drying step was used. Recoveries from a dry sorbent were not studied. The values presented represent the absolute recovery in the test case divided by the absolute recovery from the cartridge loaded and analyzed immediately. Decreasing recoveries with time are indicated. Therefore, increasing penetration of the nonpolar test compounds into the polymer structure is indicated. This effect could be greatly reduced through the use of appropriate controls.

The preliminary sampling and analysis procedure, including a drying step, was applied to test the behavior of the cartridges designed for high pressure desorption. It must be stressed that this application is qualitative in nature not only because of the problems associated with the recovery and analysis of polar compounds, but also because of the lack of confidence in the calibration for these polar compounds, as discussed above. No problems were encountered in the sampling step; flows through the sorbent cartridges remained essentially constant during the day. The chromatogram resulting from a sampling of 6 L of the air in a synthetic organic chemistry lab resulted in a large number of full-scale and off-scale peaks. A comparison of the retention time with those of standards indicated the presence of, among other things, chloroform, dichloromethane, *n*-hexane, and carbon tetrachloride at the sub-ppm level. These levels were estimated based on the known volume of air sampled and the resulting GC peak areas, which were compared to standards. All of these compounds were found in the charcoal sample at low levels. These data are briefly summarized in Table 5. It should be emphasized that the charcoal method is not normally applied to compounds present at these low levels. Although detected, the levels of the compounds were below the lowest point of the calibration curve and no concentration can be stated with any certainty. This sorbent-based approach could clearly be applied to much lower air concentrations.

The 7.5 L air sample collected from the lobby, Figure 4A, revealed far fewer components than did the lab sample. The compounds collected using charcoal were all below the limits of detection. Upon GC analysis of 10 μ l of the headspace of the applied pesticide formulation, as shown in Figure 4B, a group of compounds were detected which had the same retention and intensity distribution as a cluster of peaks observed in the SFE/GC analysis of the PI-109 cartridge. The identities of the compounds were not determined. The concentrations of these compounds are also under-represented because they were applied only during the last 2.5 hours of the 7.5 hour sample.

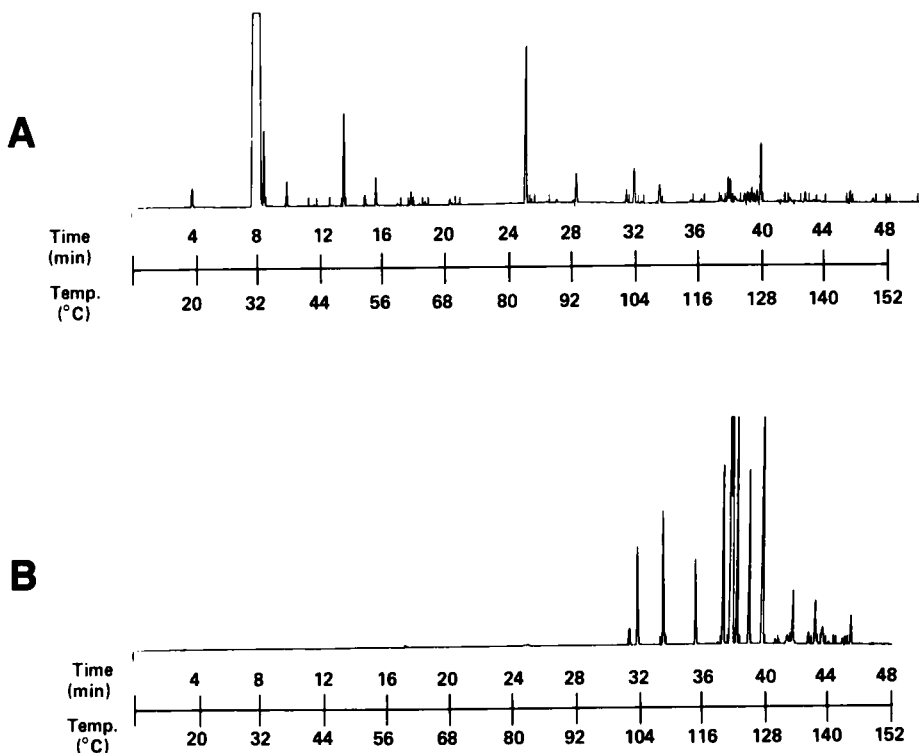


Figure 4 Chromatograms resulting from the sampling and analysis of air in a lobby during the application of pesticides (A) and the direct injection of the pesticide headspace (B).

CONCLUSIONS

The utility of SFE/thermal desorption/GC in the absence of a drying step was shown to be applicable to a wide range of volatile compounds with greatly varying polarities. Both 3A molecular sieve and AIPO-5 were shown to have very good capacities for water under supercritical fluid conditions. Preliminary experiments indicated that the molecular sieve was less adsorptive than the AIPO-5 yet, when applied to volatile components, polar compounds could not be eluted from the molecular sieve in a volume small enough to permit effective recollection of the nonpolar compounds. That is, nonpolar compounds broke through the μ -trap before polar compounds were eluted from the sieve. The limitations of the current method with polar analytes is not a result of the sorbent as detailed studies of the retentions of polar chemicals on PI-109 indicate that they are well retained.^{4,20} If an alternative or modified drying step can be found which did not adsorb the polar constituents, the method would have great utility for the analysis of toxic polar compounds in air. Efforts should be focused in this direction and on the calibration of the loading of polar standards onto the sorbent. The optimization of these aspects will result in a quantitative method for trace polar compounds. Also, SFE/GC with direct expansion on to the GC column, SFE/GC with an

intermediate trapping step, as in the current work, or directly coupled SFE/SFC can be used to access the compounds not easily handled by thermal desorption as well as those with limited volatility.

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