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Multi-adsorbent preconcentration/focusing module for portable-GC/microsensor-array analysis of complex vapor mixtures

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A small multi-adsorbent preconcentration/focusing module for a portable GC with microsensor-array detector designed to determine complex mixtures of volatile and semi-volatile organic compounds encountered in indoor working environments is described. Candidate adsorbents were assessed on the basis of analyte thermal-desorption bandwidth and efficiency, chromatographic peak shape, and breakthrough volume against mixtures of organic compounds ranging over four orders of magnitude in vapor pressure. A capillary packed with just 12.3 mg of adsorbent material comprising Carbopack B (8 mg), Carbopack X (2.5 mg) and Carboxen 1000 (1.8 mg) provided the best tradeoff in operating variables, while maintaining sufficient capacity for a 1 L air sample containing a mixture of up to 43 compounds, each at 100 parts-per-billion, at an ambient relative humidity of up to 100%. On-column focusing and temperature programming were used to enhance chromatographic separations, and detection limits as low as 100 parts-per-trillion were achieved for a 1 L air sample using an integrated array of polymer-coated surface-acoustic-wave (SAW) sensors. Implications for field analysis of indoor air quality are emphasized.

Introduction

The assessment of air quality in non-industrial working environments with low-level vapor contamination can be challenging.[1,2] Among the sources of volatile and semi-volatile organic compounds ((S)VOCs) in such environments are building and office construction materials, office furniture and equipment, human activity, personal care products, cleaning products, traffic emissions and other outdoor pollutants, and microbes.[3–5] Studies attempting to correlate contaminant levels with adverse health effects have been hampered by a lack of cost-effective on-site monitoring equipment capable of analyzing complex (S)VOC mixtures at the low concentrations prevalent in such environments.[5–8]

Measurement of indoor (S)VOCs is typically performed by sampling with canisters or multi-adsorbent sampling tubes followed by GC-MS analysis of a selected series of target analytes.[8–11] This approach is time-consuming and expensive, and provides limited temporal resolution of vapor concentrations. Real-time measurements with survey instruments employing non-specific detectors (*e.g.*, flame or photo-ionization) provide so-called ‘total’ VOC levels (TVOC).[12,13] However, TVOC concentrations are of limited value in source apportionment or health effect studies. The cost of more sophisticated instruments, such as portable GC-MS[14–16] or remote-optical FTIR spectrophotometers,[17,18] which are capable of compound-specific analysis, prohibit their routine use in such studies.

The work described here represents part of an on-going effort to develop a fieldable, near-real time analyzer for complex indoor (S)VOC mixtures. The near-term goal is to demonstrate the analysis of (S)VOC mixtures of 30 or more compounds spanning a wide range of structures and volatilities at low or sub-ppb levels within a cycle time of 10–15 min. Fig. 1 shows the key components of the instrument, whose design has been described elsewhere.[19,20] Air samples are drawn through the preconcentrator/focuser to capture the vapors, which are subsequently thermally desorbed and passed to the dual-capillary-column separation stage. The pressure control valve at the inter-column junction permits adjustment (tuning) of separations.[20–22] The array of polymer-coated surface acoustic

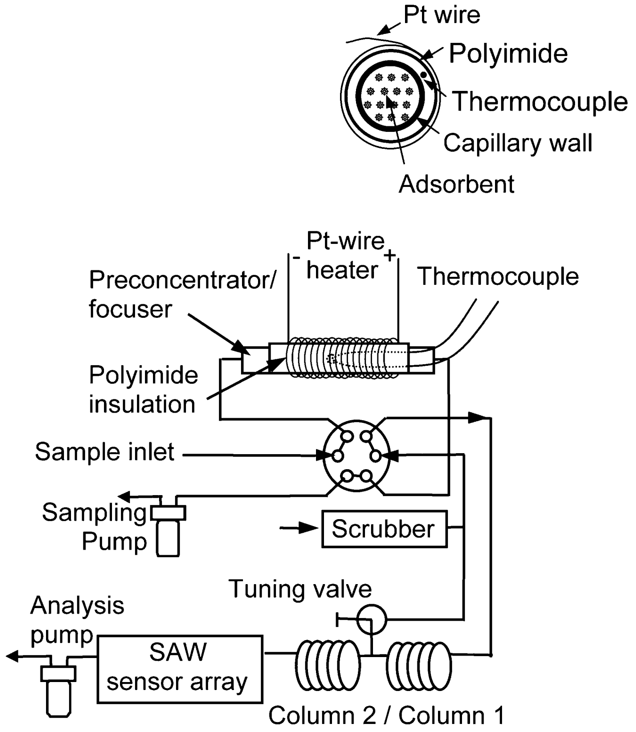

Fig. 1 Portable indoor-air quality analyzer design. Inset shows a detailed cross section of the preconcentrator/focuser assembly.

wave (SAW) sensors provides the identity (*via* pattern recognition) and quantity of eluting vapors.[23–26] Using ambient air as the carrier gas and a small vacuum pump for sample transfer reduces system size and complexity.

In order to achieve detection limits in the low or sub-ppb range while minimizing inlet band broadening for the chromatographic separation of complex mixture components, the preconcentration/focusing module must be precisely designed. The approach we have taken is similar in concept to that used in conventional sorbent-tube methods for ambient air sampling where tens-to-hundreds of mg of a low-surface-area sorbent are packed upstream from similar quantities of a higher-surface-area sorbent to trap progressively smaller and more volatile species.[9–11] In our system, however, we must minimize the adsorbent bed mass, which in turn requires a detailed analysis of both adsorption capacity and desorption efficiency.

The use of small, focusing adsorbent traps containing ~20–70 mg of adsorbent downstream from larger sampling beds has been reported,[11,27] and narrow injection bandwidths have been achieved by thermal desorption of these and similar traps.[27–30] However, published studies of such mini-traps have addressed only simple mixtures of relatively volatile compounds using arbitrary quantities of adsorbent.

In a previous study,[19] we reported on a preconcentration/focusing module for VOCs with vapor pressures ≥8 Torr, and demonstrated the analysis of a 20-vapor mixture with a standard chromatographic system having a single, polymer-coated SAW sensor as the detector. A subsequent effort showed that the distribution of vapors among several adsorbents could be adjusted by thermal modulation and/or clean-air purging of the adsorbent bed but not with a sufficiently high degree of resolution.[31] This study examines mixtures of greater complexity comprising organic compounds ranging over four orders of magnitude in vapor pressure, among which are common "signature vapors" associated with microbial sources of contamination.[3,32–34] We examine the tradeoffs among adsorption capacity and desorption bandwidth and efficiency as a function of adsorbent bed composition and vapor-mixture composition. The bandwidths of compounds eluting from the GC and measured with an FID are used as measures of preconcentrator/focuser performance. Two designs are compared: one employing two adsorbents and the other employing three adsorbents. Responses from a GC detector consisting of an integrated array of three polymer-coated SAW sensors are presented for the first time.

Experimental

Materials

The 43 compounds listed in Table 1 with their corresponding vapor pressures (p_v) were selected on the basis of their prevalence in indoor environments and their collective volatility range. Included are common solvent vapors, paint and deodorant constituents, and several compounds known to be emitted by microbial species often encountered in problem office buildings.[3,32–34] They were obtained from Aldrich (Milwaukee, WI) at ≥98% purity except for 2-methylheptane (99%) and octamethylcyclotetrasiloxane, (D4, 98%) obtained from Acros/Fisher (Pittsburgh, PA), 2-methylfuran and 2,5-dimethylfuran (99%, Lancaster, Windham, NH), 4-phenylcyclohexene (98%,Chemsampco, Trenton, NJ), and decamethylcyclopentasiloxane (D5, Gelest, Tullytown, PA).Table 2 lists the adsorbent materials and some relevant physical properties. The graphitized carbon blacks Carbotrap C, Carbopack Y, Carbopack B and Carbopack X, and the carbon molecular sieve Carboxen 1000 were obtained from Supelco (Eighty-Four, PA).

Specific surface areas and average pore sizes were measured by N_2 adsorption at 77 K on a Micromeritics ASAP 2000M analyzer (Norcross, GA) from samples degassed at 80 °C under high vacuum for 12 h prior to analysis. Specific surface areas were calculated by the multipoint BET method and pore sizes were determined from density functional theory (DFT) assuming a slit-like pore model using software provided by the manufacturer.

Preconcentrator construction

Preconcentrators were constructed from thin-walled glass (1.15 mm id) or stainless-steel (1.32 mm id) capillaries 7.5 cm in length. Packed adsorbents beds ranging in mass from 1 to 20 mg were retained with a fine stainless-steel mesh. A fine-wire thermocouple was held snugly against the outer capillary wall with a sleeve of polyimide, and Pt wire (0.13 mm diameter, 0.1 Ω cm^{-1}) was coiled around the polyimide tube to create a heated region that extended beyond the lengths of the adsorbent beds (see Fig. 1). The same Pt-wire-wrapped polyimide tube could be used repeatedly.

Test atmosphere generation

On the basis of published indoor-air quality investigations indicating that (S)VOC levels rarely exceed 100 ppb,[3–7] all tests were performed at this limiting concentration level. Test atmospheres were generated by injecting liquid solvent into a

Table 1 Volatile and semi-volatile organic compounds tested.[45]

Compound	Vapor pressure/ Torr	Compound	Vapor pressure/ Torr
Acetone[a]	231	2-Propylbenzene	5
3-Methylfuran[a]	200	α-Pinene[a]	5
Methylchloroform	124	β-Pinene[a]	5
Ethyl acetate[a]	95	n-Nonane	4.3
Benzene	95	Heptanal[a]	4
2-Butanone[a]	91	2-Heptanone[a]	3.9
1,2-Dichloroethane	88	Hexanal[a]	3
2,5-Dimethylfuran	66	d-Limonene[a]	3
Trichloroethylene	47	D4	3
2-Propanol	43	Mesitylene	2.5
2,4-Dimethylhexane[a]	35	3-Methyl-1-butanol[a]	2.4
2-Methylheptane	30	*p*-Dichlorobenzene	1.76
Toluene	28.5	D5	1.5
Perchloroethylene	18.5	3-Octanone[a]	1.4
n-Octane	14	Butoxyethanol	0.85
Butyl acetate	12	1-Octen-3-ol[a]	0.2
Chlorobenzene	11.8	n-Dodecane	0.12
Ethylbenzene	10	Naphthalene	0.08
p-Xylene	9	3-Octanol[a]	0.08
m-Xylene	8	4-Phenylcyclohexene	0.04
n-Butanol	7	n-Tridecane	0.04
Styrene	6		

[a] Compounds marked with asterisks have been associated with microbial contamination in indoor environments.[32–34]

Table 2 Adsorbent materials and selected physical properties

Adsorbent	Mesh	Specific surface area[a]/m^2 g^{-1}	Average pore size/Å
Carboxen1000	45/60	1200 (1070)	10–12 (15)
Carbopack X	40/60	250 (230)	100
Carbopack B	40/60	100	ND[b]
	60/80	100 (86)	ND[b]
Carbopack Y	40/60	25 (25)	ND[b]
Carbotrap C	20/40	10	ND[b]

[a] Values in parentheses were determined experimentally. [b] ND: Not determined.

seasoned (*i.e.*, pre-exposed and repeatedly purged until clean) Tedlar® bag pre-filled with a known volume of clean, dry dilution air from a compressed cylinder. For the more-volatile test compounds, an initial test-atmosphere of 100 ppm was generated and then 10 mL aliquots were transferred by gas-tight syringe to a second 10 L Tedlar bag. For less volatile compounds (*i.e.*, those with $p_v < 2$ Torr) samples of saturated headspace (0.4–60 mL, depending on the vapor) were transferred by gas-tight syringe to a 10 L bag and diluted to 100 ppb. The concentrations of vapors in this subset were estimated from their respective vapor pressures (Table 1) and the dilution volume assuming ideal behavior. All test atmospheres were maintained at ambient temperature, which ranged from 26 ± 2 °C.

For testing relative humidity (RH) effects, dilution air used to fill the final bag was first passed through a gas-sparging vessel containing distilled water. An additional 50 µL of distilled water was then injected into the bag to ensure that saturation was maintained over the course of the experiments, since water vapor permeates rapidly through the Tedlar bag wall.[35]

Preconcentrator performance

The apparatus used for desorption bandwidth determinations has been described previously.[19] Initial tests of individual adsorbent materials were performed using capillary bed masses of 5 mg. To expedite these tests, 0.5 mL samples of vapor at 100 ppm were injected into a metered clean-air stream drawn through the preconcentrator at 0.1 L min^{-1} by mini-diaphragm pump (UN86KTDC, KNF Neuberger , Trenton, NJ). A 1 L sample was collected, which yields the mass-equivalent of a 50 ppb L air sample. The flow through the capillary was then stopped, the heater activated, and an upstream six-port valve was actuated to backflush the desorbed sample directly to the FID of a GC (HP-6890, Agilent, Palo Alto, CA) on a background of clean, dry air from a compressed cylinder at a flow rate of 4 mL min^{-1}. The transfer line consisted of a short length of deactivated fused silica tubing (0.25 mm id).

The heater controller brought the temperature up to 300 °C within 2–3 s and maintained this temperature (±10 °C) until the observed FID signal returned to baseline. Peak width at half-height (PWHH) was used as the performance metric for comparisons among the vapor-adsorbent combinations. Desorption efficiency was determined by repeating the heating cycle immediately and comparing the magnitude of any residual FID signal to that obtained from the initial sample desorption.

Adsorption capacity was assessed in terms of the 10% breakthrough volume, V_b, defined as the volume of contaminated air required to produce a concentration of a specified vapor downstream from the preconcentrator/focuser equivalent to 10% of inlet concentration. All capacity tests were performed at a 100 ppb challenge concentration (for each component in the case of mixtures) and a flow rate of 0.1 L min^{-1}.

Pressure drop was examined as a function of adsorbent mesh size over a range of flow rates using a Magnehelic differential pressure gauge connected by a tee downstream from the preconcentrator.

SAW sensor array

An integrated array of four SAW sensors fabricated on an ST-quartz substrate was provided for this study by researchers at Sandia National Laboratories.[36,37] The array was enclosed in a 2 µL cell having inlet and outlet fused-silica capillaries. Each sensor was designed to operate at a nominal frequency of 520 MHz. The SAW phase shift for each of the three working sensors was subtracted from that of the fourth (uncoated) reference device and converted to an analogue voltage with on-chip circuitry. Output voltages were acquired at a rate of 10 Hz per sensor, passed through a 16-bit A/D converter (DAQPad-MIO-16XE-50, National Instruments, Austin, TX) and stored in a personal computer with software written in Labview (V 5.0, National Instrument).[31] The three working sensors were coated with polyisobutylene (PIB), ethyl cellulose (ECEL) or BSP3, which is a polydimethylsiloxane having hexafluorobisphenol A moieties incorporated along the backbone.[38,39] BSP3 was provided courtesy of Dr. Jay Grate from Pacific Northwest National Laboratories. The mass of coating on each sensor is that corresponding to a frequency shift of ~1 MHz.

Results and discussion

Desorption bandwidth

From our previous work, it was determined that a dual-adsorbent bed comprising 2.1 mg of Carboxen 1000 and 4.3 mg of Carbopack X provided adequate capacity and efficient, sharp desorption of mixtures containing vapors with vapor pressures ≥8 Torr in air at up to 100% RH.[19] A maximum desorption PWHH value of 3 s, which corresponds to a preconcentration factor of 5000 for a 1 L sample and a desorption flow rate of 4 mL min^{-1}, was used as a performance benchmark. Since most vapors less volatile than benzene (*i.e.*, $p_v < 95$ Torr) showed significant tailing upon desorption from Carboxen 1000, benzene served as the sentinel breakthrough vapor to determine the minimum required mass of Carbopack X. The mass of Carboxen 1000 employed was that just sufficient to avoid breakthrough of acetone in a 1 L sample in the presence of the other mixture components. Thus, vapors more volatile than benzene, or more polar but with similar volatility (*e.g.*, ethyl acetate, 2-butanone), were allowed to breakthrough to the Carboxen 1000 and the remaining vapors in the 20-vapor set were captured quantitatively on the Carbopack X. This bed could thus serve to efficiently capture and release any or all of the 20 vapors tested, and would likely serve adequately for other vapor mixtures spanning a similar range of volatility.

For addressing less volatile compounds, we sought adsorbents with lower surface areas that had thermal stabilities similar to those of the Carbopack X and Carboxen 1000, which showed reliable performance for hundreds of desorption cycles (300 °C) in air.[19] The graphitized carbons Carbopack B, Carbotrap C, and Carbopack Y were the most suitable candidates identified (see Table 2 for specific surface areas).[40–41] Carbopack X was also included in these follow-up tests. Limited testing of 60/80 mesh Carbopack B in our earlier study supported its inclusion in the current study.[19] Tenax TA and Tenax GR were not examined in detail because of their lower maximum operating temperature and greater tendency for artifact formation.[11,42]

A representative subset of five vapors (*i.e.*, α-pinene, d-limonene, 3-octanol, 4-phenyl cyclohexene, and tridecane) was selected for initial screening experiments. As shown in Fig. 2, desorption bandwidths for α-pinene are <3 s, while those for the remaining vapors are >3 s (*i.e.*, 10–30 s), from all four adsorbents. In contrast to the other adsorbents, Carbopack X retained a significant amount of residual d-limonene after an initial desorption and was therefore not tested with the less volatile compounds.

Since the desorption bandwidths showed little dependence on the adsorbent specific surface area in the range of 10–100 m^2 g^{-1} (Fig. 2), the option of installing yet a smaller downstream focusing trap was not pursued. Instead, on-column focusing was explored as a means to reduce the inlet bandwidth to the GC column for the less volatile compounds in the test set. A 15 m capillary column (DB-5, 0.25 mm id, 0.25 µm, Supelco) was placed between the preconcentrator and FID. The column was maintained at 35 °C for 1.5 min and then ramped to 140 °C at 20 °C min^{-1}. Note that the low-temperature segment of the temperature program enhances the separation of more-volatile vapors, while also focusing the less volatile vapors in a very narrow section at the head of the column, and so fits well within the overall analytical scheme for complex-mixture analysis.

Fig. 3a shows the FID profile for tridecane, the least volatile analyte tested, desorbed directly from the preconcentrator packed with 5 mg of Carbopack B (60/80). The PWHH value is 26 s (Fig. 2) and it required 90 s of heating to regain the baseline (note: the FID trace reflects the fluctuations in the heater controller). Fig. 3b shows the dramatic effect of on-column focusing: the post-column PWHH value for tridecane is only 1.8 s.

All three of the low-surface-area graphitized-carbon adsorbents gave 100% desorption efficiency for the vapors in the test set under these desorption conditions (300 °C for 90 s at 4 mL min^{-1}) and there was no difference among these adsorbents in the length of time at 300 °C required for complete desorption of the tridecane. The length of time required for desorption thus appears to be a function of compound volatility rather than the strength of the vapor-adsorbent interactions. Although this suggests that rapid initial heating of the preconcentrator would not be necessary, it is critical for efficient separation of the more volatile vapors that do not benefit from on-column focusing even at the low initial column temperature employed. All subsequent testing of desorption bandwidth was performed with a 15 m GC column in-line.

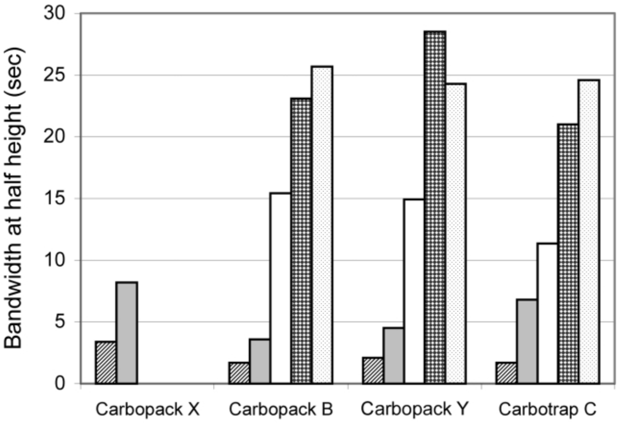

Fig. 2 Values of PWHH (FID) for a subset of compounds desorbed at 300 °C and 4 mL min^{-1}. Compounds tested (bars) are, from left to right, α-pinene, d-limonene, 3-octanol, 4-phenylcyclohexene, and tridecane. Carbopack X was tested only with α-pinene and d-limonene (see text).

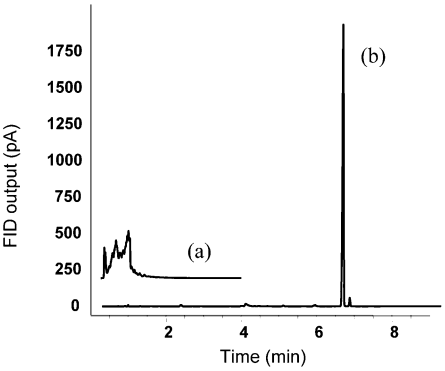

Fig. 3 Effect of on-column focusing: (a) FID response upon desorption of tridecane directly from preconcentrator/focuser; (b) FID response to tridecane after on-column focusing and temperature-programmed elution from a 15 m capillary column.

Reducing the bandwidths of GC peaks allows greater resolution of complex mixture components and also reduces detection limits *via* improvements in signal:noise ratios. Table 3 shows the PWHH values for an expanded subset of test compounds upon desorption from each of three of the graphitized carbons and from Carboxen 1000, followed by GC separation under the conditions given above. Carbotrap C was excluded on the basis of the results presented in Fig. 2. In general, desorption from an adsorbent with lower surface area provides sharper GC peaks, but the effect decreases with decreasing analyte volatility. For this data set, the effect becomes negligible for compounds less volatile than d-limonene (*i.e.*, $p_v \leq 3$ Torr) and an adsorbent surface area < 100 m^2 g^{-1}.

Although GC-elution PWHH values < 3 s are obtained for acetone and benzene from Carboxen 1000 their PWHH values are even narrower from the lower-surface-area Carbopack X. Similarly, among the five moderately volatile vapors (benzene, toluene, *m*-xylene, α-pinene, and d-limonene), desorption from the Carbopack B consistently generates narrower peaks than from Carbopack X. The relatively broad PWHH values for *m*-xylene and α-pinene from Carbopack B, compared to the less volatile test compounds, indicates that on-column focusing is less significant for these two compounds under these temperature programming conditions. Among the three least volatile compounds (d-limonene, D5, and tridecane) there is no significant difference in PWHH between Carbopack B and Carbopack Y (and Carbotrap C, see above) despite the 4-fold difference in specific surface area of the adsorbents.

Thus, for analysis of the less volatile compounds the desorption band width is not important and on-column focusing plays a major role in defining peak shape, while for the more volatile compounds the desorption band width is very important and the nature of the adsorbent plays a major role in defining peak shape. Peaks for moderately volatile compounds are the broadest because they are too volatile to benefit from on-column focusing yet not volatile enough to avoid some degree of band broadening during thermal desorption. Peak broadening of moderately volatile vapors will be observed generally, but will be affected by GC conditions.

Adsorption capacity and optimized bed masses

Although the immediate goal was to demonstrate the analysis of a 30-vapor mixture, in practice one must account for the possible presence of non-target vapors that will occupy adsorption sites and reduce capacity for the target vapors. To address this we chose several additional compounds to include in the test set that have been found as contaminants in indoor air and that collectively span a range of structures and volatilities. This brought the total set of test compounds to 43, or a 40%

Table 3 Vapor bandwidths (PWHH/s) after eluting from the GC column as a function of adsorbent in preconcentrator/focuser

Adsorbent	Acetone	Benzene	Toluene	*m*-Xylene	α-Pinene	d-Limonene	D5	Tridecane
Carboxen 1000	1.5	2.7	3.6					
Carbopack X	0.8	1.4	2.1	3.0	2.6	3.1[a]		
Carbopack B	0.8	1.5	2.2	2.2	1.7	1.9	1.7	
Carbopack Y						1.7	1.9	1.8

[a] Incomplete desorption.

excess. Designing the preconcentration/focusing module to provide sufficient capacity to trap all of these compounds at 100 ppb is therefore quite conservative, since fewer compounds are often encountered and vapor concentrations are typically much lower in indoor working environments. The decision to use a 1 L sample volume was made on the basis of earlier tests of sensor sensitivity,[19] and in consideration of instrument duty cycle—this sample volume can be collected within a few minutes with portable sampling pumps that typically operate at flow rates of 0.1–0.3 L min^{-1}.

From the results of the desorption tests, Carboxen 1000, Carbopack X, and Carbopack B were selected for further testing. Since desorption peaks from Carbopack B and Carbopack Y are similar, the larger surface area of the Carbopack B favors its use for trapping less volatile compounds. The dependence of the GC elution peak width on the nature of the adsorbent for the more volatile compounds suggested using a lower-surface-area adsorbent where possible within the constraints of capacity requirements. Issues that remained to be addressed included adsorption capacity, pressure drop, and humidity effects.

Several of the more volatile compounds in Table 1 have very small breakthrough volumes with Carbopack X and Carbopack B. Therefore, Carboxen 1000 would be required in any final preconcentrator/focuser module. Since many of the less volatile compounds were desorbed from Carbopack X at less than 100% efficiency, a certain mass of Carbopack B would be required. This raised the question of whether Carbopack X would be required at all. In other words, would a 2-adsorbent bed of Carboxen 1000 and Carbopack B suffice or would a 3-adsorbent bed containing all of these adsorbents be preferable? In either case, the minimum adsorbent mass needed to be determined.

The adsorption capacity of Carbopack B (60/80) was assessed first by drawing test-atmospheres of the 43-vapor mixture through capillaries packed with different masses of adsorbent and analyzing the downstream air by GC-FID. Fig. 4 shows the linear dependence of the 10% V_b value on bed mass for each of three possible sentinel breakthrough compounds for the Carbopack B: benzene, toluene, and α-pinene. For a 1 L sample volume, required masses are 20, 8, and 4 mg, respectively.

At this point it became apparent that the mesh size of the 60/80 Carbopack B was a limiting factor. Bed masses >10 mg limited the flow rate achievable with the instrument sampling pump to <0.1 L min^{-1}—the pressure drop across the capillary packed with 10 mg at 0.1 L min^{-1} was ~9 psi. Substituting a larger mesh of Carbopack B (*i.e.*, 40/60) reduced the pressure drop by >3-fold and permitted higher flow rates and larger bed masses to be considered. Tests with toluene vapor were performed to confirm that there were no differences in adsorption capacity (10% V_b) or desorption bandwidth (PWHH) between the two mesh sizes of Carbopack B (note: similar tests of capacity and desorption band width as a function of mesh size with Carboxen 1000 and Carbopack X showed them also to be independent of particle size).

In consideration of the 3-adsorbent configuration that included Carbopack X, toluene was chosen as the sentinel breakthrough vapor for Carbopack B, with the remaining vapors being allowed to pass to the downstream adsorbents. A series of capillaries was packed with 8 mg sections of Carbopack B and varying amounts of Carbopack X downstream. Benzene was selected as the sentinel breakthrough vapor for the Carbopack X bed on the basis of the data in Table 2 and previous results.[19] Fig. 5 shows the relationship between the Carbopack X mass and V_b for benzene when challenged with the 43-vapor mixture with 8 mg of Carbopack B upstream. As shown it requires 2.5 mg of Carbopack X to achieve a benzene V_b of 1 L. The same test was then performed at 100% RH and no effect was observed on V_b for benzene (*i.e.*, V_b = 1.03 and 1.04 L, at 0% and 100% RH, respectively).

Tests were then extended to include Carboxen 1000 downstream from the Carbopack X in the preconcentrator/focuser capillary using acetone as the sentinel breakthrough vapor. To address the known affinity of Carboxen 1000 for water vapor,[31,43,44] tests were performed at 100% RH. It was found that 1.8 mg was required to obtain a 1 L V_b for acetone (Fig. 5). The total mass of this optimized 3-adsorbent configuration is therefore 12.3 mg—breakthrough volumes are shown as a function of adsorbent mass in Fig. 5 and the distribution of vapors among the adsorbents is shown in Fig. 6. This provides sufficient capacity for 43 compounds at 100 ppb with a sample volume of 1 L and also permits efficient desorption at 300 °C.

Returning to consider the 2-adsorbent configuration, benzene was used as the sentinel breakthrough vapor for determining the required mass of Carbopack B in this case because compounds breaking through Carbopack B after benzene had very broad desorption peaks from Carboxen 1000 (see toluene entry in Table 3, for example). The preceding analyses indicated the need for an upstream bed containing 20 mg of Carbopack B. Subsequent tests with Carboxen 1000 showed that 2.0 mg of this adsorbent was required to maintain an acetone V_b of 1 L at 100% RH. Note that the 3-adsorbent design requires about half of the total mass of the 2-adsorbent design because of the greater efficiency of the Carbopack X for capturing the moderately volatile vapors.

Fig. 7 compares the performance of these two preconcentrator/focuser configurations in terms of the normalized GC-FID peak height values for selected vapors. The ratio of the peak height to the peak area was used as the normalized metric to account for slight differences in injection volume (mass). In

Fig. 4 Dependence of 10% breakthrough volume on mass of Carbopack B for the sentinel compounds benzene (triangles), toluene (squares), and α-pinene (circles) when challenged with the 43-component mixture at component concentrations of 100 ppb.

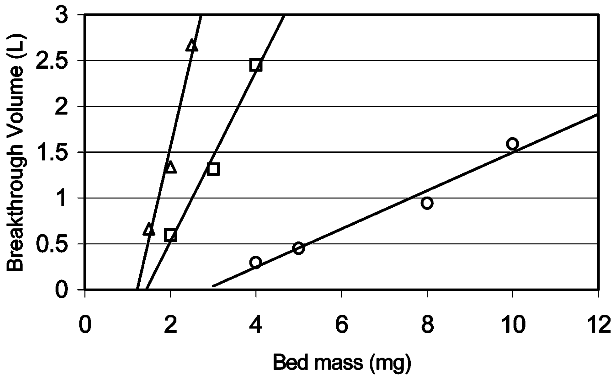

Fig. 5 Dependence of 10% breakthrough volumes on adsorbent mass for each stage of the 3-stage preconcentrator/focuser design (43-component mixture at 100 ppb each): acetone-Carboxen 1000 (triangles); benzene-Carbopack X (squares); and toluene-Carbopack B (circles).

both configurations, most compounds less volatile than trichloroethylene are trapped completely by Carbopack B. Accordingly, no difference in normalized peak height is observed between the two configurations (see toluene in Fig. 7, for example). Notably, the lack of any significant difference in normalized peak height among these vapors indicates that the larger bed mass of the 2-adsorbent configuration does not adversely affect the desorption bandwidth. In both configurations, acetone and 2-propanol are retained primarily on the Carboxen 1000 leading again to similar peak heights.

Significant differences are seen for the vapors that are distributed among different adsorbents in each configuration. Predictably (Fig. 2), the benzene peak is about 25% sharper using the 2-adsorbent configuration because it is completely trapped on (and desorbed from) the lower-surface-area Carbopack B, whereas in the 3-adsorbent configuration a significant fraction of the benzene is trapped on (and desorbed from) the Carbopack X. The broadening of the peak reflects the slower desorption from a larger-average-surface-area adsorbent. The trichloroethylene data can be explained similarly, though the effect is smaller because more is retained on the Carbopack B in the 3-adsorbent design.

For 2-butanone, 2-methylfuran, ethyl acetate, and dichloroethane, the 3-stage design outperforms the 2-stage design by a fairly wide margin. In the 2-stage design, these vapors are trapped primarily on the high-surface-area Carboxen 1000 whereas in the 3-stage design they are divided between Carboxen 1000 and Carbopack X. Methyl chloroform represents a unique case where the retention on Carboxen 1000 is apparently so different from that on Carbopack X as to produce two partially resolved peaks upon desorption from the 3-stage design and elution through the GC. It also appears that at this concentration and sample volume nearly equal fractions of the vapor sample are captured on the two adsorbents (see below). Note, however, that despite the differences in performance between these two preconcentrator/focuser configurations, the GC-elution PWHH values are < 3 s in all cases.

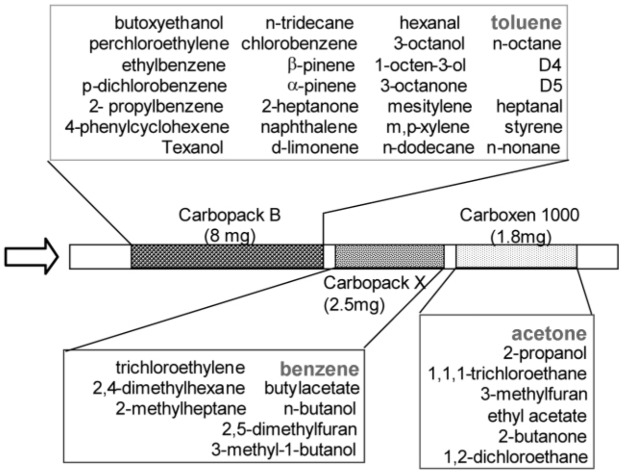

Fig. 6 43-vapor mixture distribution within the multi-adsorbent preconcentrator/focuser. Vapors shown in bold font are the sentinel breakthrough vapors for each adsorbent. Arrow shows direction of vapor loading.

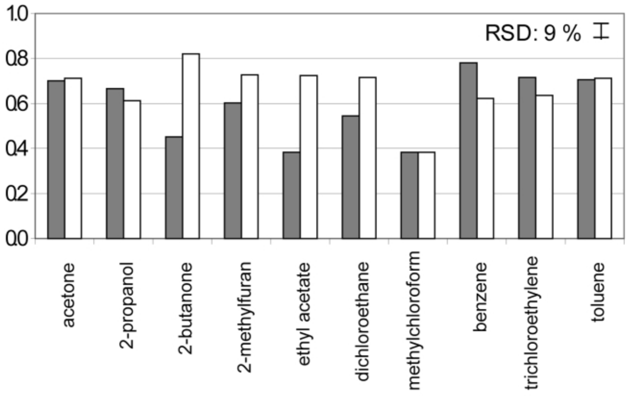

Fig. 7 Normalized desorption peak height comparisons between 2-stage (shaded) and 3-stage (unshaded) preconcentrator/focuser designs. Error bar represents the average relative standard deviation (~9%) determined from replicate measurements of a subset of five of the vapors.

Effect of vapor-loading on peak shape

Since peak shape can vary with the trapping adsorbent for the more volatile compounds, and some displacement from one adsorbent to the next may occur as a function of sample composition and concentration, it was of interest to explore the extent of the effect this factor might have on peak shape for the 3-stage design. Toward this end, 100 ppb samples of increasing volume (from 0.2 to 1 L), corresponding to proportional increases in mass loading, were analyzed for each of four vapors: acetone, ethyl acetate, benzene, and toluene. Normalized peak heights (*i.e.*, height/area) for acetone and toluene were unaffected because they are trapped on a single adsorbent in all cases. For benzene and ethyl acetate, however, large changes are observed as the fractional distribution of the sample shifts from Carbopack B to Carbopack X. This leads to distortions in the plots of peak height *versus* injection volume, and will affect estimates of detection limits. Peak areas were unaffected by this phenomenon, and plots of peak area *versus* injection volume were linear in all cases.

Testing with the SAW sensor array

In the portable instrument being developed (Fig. 1), an array of SAW sensors will be used for vapor recognition and quantification. To assess the response characteristics of the sensor array using the 3-stage preconcentrator and the 15 m GC column, tests were performed by splitting the column output, with half directed to the FID and the other half to the SAW sensor array. Fig. 8 shows the chromatograms for a 15-component mixture containing compounds that span the volatility range of the entire 43-vapor set, from acetone (p_v = 231 Torr) to tridecane (p_v =

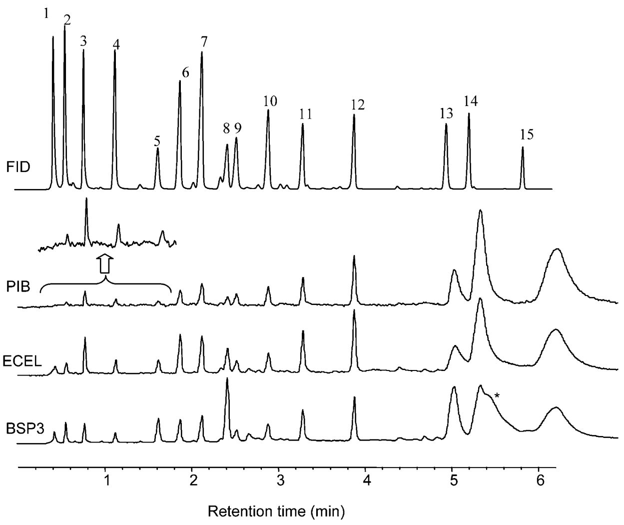

Fig. 8 Chromatograms of a 15-compound mixture desorbed from the optimal 3-stage preconcentrator/focuser and detected with an FID (upper trace) and a SAW sensor array (lower three traces). Peak assignments: 1 acetone, 2 ethyl acetate, 3 trichloroethylene, 4 toluene, 5 butyl acetate, 6 chlorobenzene, 7 *m*-xylene, 8 2-heptanone, 9 nonane, 10 α-pinene, 11 mesitylene, 12 d-limonene, 13 D5, 14 dodecane, 15 tridecane.

0.04 Torr). For the purposes of clarity the concentrations of the less volatile compounds were increased and those for the less volatile compounds were decreased in the test-atmosphere used to generate these data. In addition, the scales on the traces have been adjusted to facilitate comparison among the outputs.

The FID trace serves as a reference. For the first 12 eluting peaks, the PWHH values measured from the sensors in the array are almost identical to those from the FID meaning that there is no loss in chromatographic resolution. However, for the last three eluting compounds (*i.e.*, D5, dodecane, and tridecane) the sensors yield very broad peaks with increased retention times. Two factors contribute to these results. The SAW sensor array is operated at room temperature and is connected to the GC column by ~30 cm of passivated fused silica capillary (0.25 mm id), most of which is at room temperature. Wall adsorption along the capillary and possibly within the array housing, coupled with the finite vapor sorption/desorption kinetics in the polymeric sensor coatings will lead to peak broadening such as that observed. The BSP3-sensor peak eluting on the downstream shoulder of the dodecane is an artifact of unknown origin. Although reproducible, it was not observed with the other sensors or the FID.

As expected for sorption-based sensors, there is a general increase in sensitivity with decreasing analyte vapor pressure (*i.e.*, increasing GC retention time), which is evident in spite of the adjustment made in test-atmosphere concentrations. The sensitivity of the BSP3-coated SAW sensor is consistently greater than those of the PIB- and ECEL-coated sensors (note: the PIB and ECEL traces in Fig. 8 have been amplified by 3.2× and 6.7×, respectively). The selectivity of the hydrogen-bond-acidic BSP3-coated sensor for compounds with hydrogen-bond basic functional groups,[39] such as butyl acetate and 2-heptanone, is evident from the larger relative responses for these vapors.

The limits of detection for the FID are consistently lower than those for any of the SAW sensors. However, for the 1 L sample volumes employed, LODs for the BSP3 sensor range from 3 ppb for acetone to 0.10 ppb for 2-heptanone, and are <1 ppb for most compounds. These are adequately low for the intended application. The PIB-coated sensor provides the highest LODs, with those for acetone and ethyl acetate being >90 ppb, while those for the remaining vapors are <25 ppb and are <10 ppb in most cases.

The tradeoff for the reduced sensitivity with the sensor array (relative to the FID) is the potential for vapor recognition from the differential response patterns obtained for each vapor. The combination of unique response patterns and retention times is a very powerful qualitative tool. With just the three sensors in this array, it is evident that the pattern of responses for many of the vapors are quite different (compare the BSP3 : ECEL : PIB peak-height ratios for 2-heptanone to those for nonane, for example). Thus, by creating a library of patterns and retention times, vapor recognition is quite straightforward and overlapping peaks should be resolvable by pattern recognition in many cases. A more detailed analysis of vapor recognition, coupled with tunable retention will be provided in a subsequent publication.

Conclusion

This study has illustrated that the inherent tradeoff between adsorption capacity and desorption efficiency/bandwidth can be addressed to produce an adsorbent that serves as both a preconcentrator and focuser for complex mixtures of vapors. Thus, a 3-stage adsorbent bed containing just 12.3 mg of adsorbent can efficiently trap and thermally desorb up to 43 vapors, spanning four orders of magnitude in vapor pressure, at concentrations as high as 100 ppb. Although designed using a specific set of test compounds, this preconcentrator/focuser should be suitable for other complex mixtures of volatile and semi-volatile compounds as well. The procedure presented for optimizing the design should also be broadly applicable.

For volatile compounds the nature of the adsorbent is critical in determining the desorption bandwidth and subsequent chromatographic resolution. For less volatile vapors (*i.e.*, those with p_v below ~3 Torr) it is not possible to generate a desorption bandwidth narrow enough for efficient chromatography without relying on on-column focusing. The latter technique works quite well, however, and the results presented have demonstrated that semi-volatile organic compounds can be analyzed without the need for cryogenic focusing, which would be infeasible in a portable system.

Preliminary test results using this preconcentrator/focuser in conjunction with a conventional GC column and a novel, integrated SAW sensor array developed at Sandia National Laboratories[36,37] have demonstrated that the preconcentration factors achieved are adequate for many indoor air quality applications. To our knowledge this is the first published report on the use of GC with a polymer-coated SAW sensor array for the quantitative analysis of complex mixtures of organic vapors.

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References

1 L. E. Ekberg, in *Organic Indoor Air Pollutants—Occurrence, Measurement, Evaluation*, ed. T. Salthammer, Wiley-VCH, Weinheim, FRG, 1999, pp. 73–83.
2 B. Burton, in *Volatile Organic Compounds In Indoor Air Pollution and Health*, ed. E. Bardana, Jr. and A. Montanaro, Marcel Dekker, New York, 1997, pp. 127–153.
3 P. Wolkoff, *Indoor Air*, 1995, suppl. 3, 9.
4 S. Brown, M. Sim, M. Abramson and C. Gray, *Indoor Air*, 1994, **4**, 123.
5 R. D. Edwards, J. Jurvelin, K. Koistinen, K. Saarela and M. Jantunen, *Atmos. Environ.*, 2001, **35**, 4829.
6 J. T. Brinke, S. Selvin, A. T. Hodgson, W. J. Fisk, M. J. Mendell, C. P. Koshland and J. M. Daisey, *Indoor Air*, 1998, **8**, 140.
7 P. Wolkoff and G. D. Nielsen, *Atmos. Environ.*, 2001, **35**, 4407.
8 M. R. Van Winkle, *Indoor Air*, 2001, **11**, 49.
9 E. Woolfenden, *J. Air Waste Manage. Assoc.*, 1997, **47**, 20.
10 C. Y Peng and S. Batterman, *J. Environ. Monit.*, 2000, **2**, 313.
11 US EPA, TO-17, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, 2nd edn., Report No. EPA/625/R-96/010b, US Environmental Protection Agency, Washington DC, 1997.
12 S. Batterman and C. Y. Peng, *Am. Ind. Hyg. Assoc. J.*, 1995, **56**, 55.
13 M. V. Jokl, *Build. Environ.*, 2000, **35**, 677.
14 J. A. Syage, B. J. Nies, M. D. Evans and K. A. Hanold, *J. Am. Soc. Mass Spectrom.*, 2001, **12**, 648.
15 B. A. Eckenrode, *J. Am. Soc. Mass Spectrom.*, 2001, **12**, 683.
16 H. V. Piltingsrud, *Am. Ind. Hyg. Assoc. J.*, 1997, **58**, 564.
17 A. C. Drescher, D. Y. Park, M. G. Yost, A. J. Gadgil, S. P. Levine and W. W. Nazaroff, *Atmos. Environ.*, 1997, **31**, 727.

18 J. W. Childers, E. L. Thompson, D. B. Harris, D. A. Kirchgessner, M. Clayton, D. F. Natschke and W. J. Phillips, *Atmos. Environ.*, 2001, **35**, 1923.

19 C.−J. Lu and E. T. Zellers, *Anal. Chem.*, 2001, **73**, 3449.

20 J. J. Whiting, C.-J. Lu, E. T. Zellers and R. D. Sacks, *Anal. Chem.*, 2001, **73**, 4668.

21 A. J. Grall, E. T. Zellers and R. D. Sacks, *Environ. Sci. Technol.*, 2001, **35**, 163.

22 R. D. Sacks, C. Coutant and A. J. Grall, *Anal. Chem.*, 2000, **72**, 524A.

23 J. Park, W. A. Groves and E. T. Zellers, *Anal. Chem.*, 1999, **71**, 3877.

24 J. Park, G. Z. Zhang and E. T. Zellers, *Am. Ind. Hyg. Assoc. J.*, 2000, **61**, 192.

25 R. McGill, V. Nguyen, R. Chung, R. Shaffer, D. DiLella, J. Stepnowski, T. Mlsna, D. Venesky and D. Dominguez, *Sens. Actuators, B*, 2000, **65**, 10.

26 J. W. Grate, *Chem. Rev.*, 2000, **100**, 2627.

27 S. Mitra and C. Feng, *J. Chromatogr., A*, 1998, **805**, 169.

28 E. T. Zellers, M. Morishita and Q. Y. Cai, *Sens. Actuators, B*, 2000, **67**, 244.

29 W. Frank and H. Frank, *Chromatographia*, 1990, **29**, 571.

30 S. Mitra and C. Yun, *J. Chromatogr.*, 1993, **648**, 415.

31 C.-J. Lu, PhD Thesis, University of Michigan, Ann Arbor, 2002.

32 D. Norback, G. Wieslander, G. Strom and C. Edling, *Indoor Air*, 1995, **5**, 166.

33 A. −L. Pasanen, S. Lappalainen and P. Pasanen, *Analyst*, 1996, **121**, 1949.

34 A. −L. Pasanen, A. Korpi, J.-P. Kasanen and P. Pasanen, *Environ. Int.*, 1998, **24**, 703.

35 W. A. Groves and E. T. Zellers, *Am. Ind. Hyg. Assoc. J.*, 1996, **57**, 257.

36 E. J. Heller, V. M. Hietala, R. J. Kottenstette, R. P. Manginell, C. M. Matzke, P. R. Lewis, S. A. Casalnuovo and G. C. Frye-Mason, *Proc. Electrochemical Society, Volume 99-23*, ed. M. Butler, N. Yamazoe, P. Vanysek and M. Aizawa, ECS, Inc., Pennington, NJ, 1999, pp. 138–142.

37 G. Frye-Mason, R. J. Kottenstette, P. R. Lewis, E. J. Heller, R. P. Manginell, D. R. Adkins, D. Dullock, D. Martinez, D. Sasaki, C. Mowry, C. Matzke and L. Anderson, *Proceedings of Micro Total Analysis Systems 2000*, Kluwer Academic Publishers, Dordrecht, Netherlands, 2000, pp. 229–232.

38 J. W. Grate, S. J. Patrash and S. N. Kaganove, *Anal. Chem.*, 1999, **71**, 1033.

39 J. W. Grate, S. N. Kaganove, S. J. Patrash, R. Craig and M. Bliss, *Chem. Mater.*, 1997, **5**, 1201.

40 E. Matisova and S. Skrabakova, *J. Chromatogr., A*, 1995, **707**, 145.

41 M. Harper, *J. Chromatogr., A.*, 2000, **885**, 129.

42 P. A. Clausen and P. Wolkoff, *Atmos. Environ.*, 1997, **31**, 715.

43 W. A. McClenny, K. D. Oliver and E. H. Daughtrey, *J. Air Waste Manage. Assoc.*, 1995, **45**, 792.

44 J. Gawlowski, T. Gierczak, E. Pietruszynska, M. Gawrys and J. Niedzielski, *Analyst*, 2000, **125**, 2112.

45 *Handbook of Physical Properties of Organic Chemicals*, ed. P. H. Howard and W. M. Meylan, Lewis, New York, 1997.