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A Dual-Adsorbent Preconcentrator for a Portable Indoor-VOC Microsensor System

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The development and testing of a miniature dual-adsorbent preconcentrator for a microsensor-based analytical system designed to determine complex volatile organic chemical (VOC) mixtures encountered in indoor working environments at low part-per-billion levels is described. Candidate adsorbents were screened for thermal-desorption bandwidth and breakthrough volume against 20 volatile organic vapors and subsets thereof as a function of several relevant variables. A glass capillary (1.1 mm i.d.) packed with 3.4 mg of Carbopack X and 1.2 mg of Carboxen 1000 provides sufficient capacity for a 1-L dry-air sample containing all 20 vapors at concentrations of 100 ppb as well as providing a composite half-height peak width of <3 s at a desorption temperature of 300 °C and a flow rate of 4 mL/min. Required adsorbent masses increase to 7.0 and 1.5 mg, respectively, for the same mixture at component concentrations of 1 ppm. Vapor breakthrough volumes for the Carbopack X are unaffected by humidity from 0 to 100%RH, but those for the Carboxen 1000 are significantly reduced, requiring an additional 0.9 mg of the latter to avoid premature breakthrough at the 100 ppb level. Good peak shapes, efficient chromatographic separation of preconcentrated sample mixture components, and detection limits in the low-parts-per-billion range using an integrated surface-acoustic-wave (SAW) sensor are achieved. Preconcentrator design and operating parameters are considered in terms of the vapor bed-residence times and breakthrough volumes in the context of the modified Wheeler equation.

The determination of volatile and semivolatile organic compounds (VOCs and SVOCs) in nonindustrial working environments is challenging because of the low concentrations and diversity of compounds potentially encountered (typically < 100 ppb).[1−3] Currently available portable direct-reading instruments lack the sensitivity or selectivity to provide meaningful data for correlating human exposure levels with potential health effects.[4]

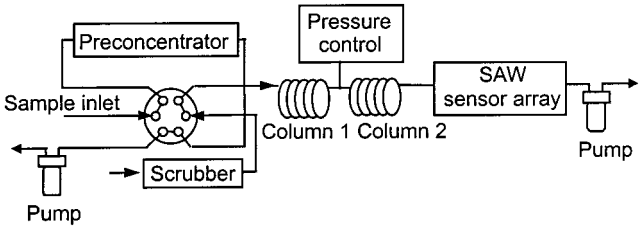

Figure 1. Key components of the microsensor system.

As a result, investigations of (S)VOC contamination in buildings generally rely on whole-air or adsorbent-tube sampling followed by laboratory GC/MS analysis.[3,5] Multiadsorbent samplers are used because of the need to capture vapors spanning a wide range of volatility and functionality.[6−8] For practical reasons, investigative studies will often target from 10 to 40 selected compounds and determine their presence or absence at concentrations above about 1 ppb.[1,2,9]

The availability of portable instrumentation capable of near-real-time determinations of specific (S)VOC concentration profiles would enhance the effectiveness of indoor air quality (IAQ) assessments and interventions.[1−3] This report describes one component of a study aimed at developing such a field-portable (i.e., laptop-computer-sized) instrument. Figure 1 shows the key components of the system being developed. The performance of the instrument relies on the functional integration of these system components, whereby the analytical burden is distributed among a multibed preconcentrator module, a dual-column separation module with tunable and programmable retention characteristics, and a detector module comprising an integrated array of polymer-coated surface-acoustic-wave (SAW) sensors.[10−14] The ultimate

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goal is to develop the capability to sample and analyze mixtures of ≥30 (S)VOCs of arbitrary composition at concentrations as low as a few ppb in under 10 min and to use response patterns from the sensor array along with chromatographic retention times to identify and quantify the vapors.[11,15−18]

Preconcentration allows the collection of enough sample mass to obtain detectable signals from the sensor array and can provide some degree of humidity compensation.[16,19−23] Since no separate focusing stage is employed in this instrument, the size of the bed must be limited to avoid excessive inlet band broadening, which would degrade chromatographic separation efficiency. The competing needs for adequate capacity, rapid desorption, compatibility with other system components, and portable operation demand optimizing the system preconcentrator. Although a number of reports have appeared on so-called microtraps comprising small adsorbent beds as potential replacements for cryogenic focusing stages for GC analysis,[24,25] none of these studies has attempted to use the same bed both for sampling large air volumes and for focusing the vapors for injection onto the GC column. Solid-phase microextraction (SPME) fibers coated with porous polymers allow for direct injection of adsorbed vapor samples, but they have severely limited capacities and do not appear to be suitable for sampling complex VOC mixtures.[26]

In this article, we describe the modeling, design, and testing of the microsensor-based analytical system preconcentrator for VOCs. Extension of the design to also address SVOCs will be reported subsequently. A conventional capillary gas chromatographic system with a flame ionization detector (GC-FID) was used for most of the experiments; however, preliminary data were also collected using a SAW sensor array as the detector. Results of tests aimed at screening a series of candidate adsorbents from an initial set of possibilities are presented, followed by determinations of optimal bed masses and assessments of humidity effects, chromatographic efficiencies, sensor responses, medium-term aging, and modeling results.

Modeling Breakthrough Volume and Residence Time. In designing the preconcentrator module for this application, a number of issues must be addressed that are not generally considered in developing sorbent-tube sampling methods in which laboratory analysis is performed using large thermal desorption units and desorbed vapors can be focused, cryogenically or otherwise, prior to analysis. In those methods, beds comprising several hundred milligrams of adsorbent and desorption times on the order of several minutes are typically required.[27−29] For the current application, although the preconcentrator must have sufficient adsorbent mass to ensure quantitative trapping of vapors in the sample stream, it is important to minimize the bed mass in order to minimize the bandwidth of desorbed vapor pulses delivered to the separation column. For less volatile vapors, some degree of focusing can be achieved on-column by maintaining an initially low column temperature,[30] but for VOCs with vapor pressures above ∼1 Torr, this is not generally possible. Other issues relevant to the design of a portable system include the heating rate achievable (if battery power is employed) and the sampling flow rate achievable with a portable diaphragm pump which, in turn, depends on the pressure drop through the preconcentrator adsorbent bed.

The vapor adsorption capacity is the overriding performance parameter, since complete removal of vapors from the sample stream is desired for quantitative analysis of vapor concentrations. The modified Wheeler model relates several important design and performance parameters to the vapor retention capacity of a granular adsorbent bed under a continuous vapor challenge.[31−34] It is derived from a mass balance between vapor entering, retained within, and exiting the bed. Most applications of this model have been concerned with determining the service lives of air-purifying respirator cartridges packed with activated charcoal or some other adsorbent;[32,35,36] however, it has also been employed to characterize adsorbent samplers[34] and preconcentrators for systems similar to that described here.[21,23]

The time required for a certain fractional breakthrough (typically, 1 or 10%) to occur can be described by the model as follows:[36]

$$t_b = \frac{\rho_b W_e}{C_0}\left[\tau - \frac{1}{k_v}\ln\left(\frac{C_0}{C_x}\right)\right] \qquad (1)$$

where t_b is the breakthrough time (min), ρ_b is the packed-bed density (g/cm^3), W_e is the kinetic adsorption capacity (g/g), $\tau = W_b/(\rho_b Q)$ is the bed residence time (min), Q is the volumetric flow rate (cm^3/min), W_b is the bed mass (g), k_v is the kinetic rate constant (min^{-1}), C_0 is the inlet concentration (g/cm^3), and C_x is the outlet concentration (g/cm^3). The variables W_e and k_v vary directly with C_0 and can be determined by a number of different approaches.[32]

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Table 1. Target Vapors, Vapor Pressures at 25 °C, and Limits of Detection (LOD) Using a Polymer-Coated SAW Sensor as GC Detector[a]

	compound	p_v[b], Torr	LOD, ppb		compound	p_v[b], Torr	LOD, ppb
1	acetone	231	7.4	11	2,4-dimethylhexane	35	7.8
2	2-propanol	43	3.5	12	toluene	28	2.9
3	2-butanone	91	2.5	13	2-methylheptane	30	3.9
4	2-methylfuran	139	9.9	14	perchloroethylene	18	1.7
5	ethyl acetate	95	1.6	15	*n*-octane	14	4.0
6	1,2-dichloroethane	88	10.3	16	butyl acetate	12	0.5
7	1,1,1-trichloroethane	124	10.2	17	chlorobenzene	12	1.6
8	benzene	95	11.1	18	ethylbenzene	10	1.9
9	trichloroethylene	47	6.1	19	*p*-xylene	9	1.2
10	2,5-dimethylfuran	66	6.1	20	*m*-xylene	8	1.2

[a] 1-L preconcentrated samples. [b] p_v = vapor pressure.

Eq 1 shows that the breakthrough time will decrease in proportion to the bed residence time over most of the useful range of bed residence times. The critical bed residence time τ_c, determined at $t_b = 0$, varies inversely with the inherent affinity of the adsorbent for the vapors and the flow rate through the bed, and provides a relative measure of vapor adsorption efficiency among different adsorbent materials.[36] For a given flow rate, bed density, and bed diameter, this also defines the critical bed length (mass).

Although t_b determinations are important in preconcentrator development,[21,23] the performance parameter of more general interest is the breakthrough volume, V_b, which is related to τ and the other design and operating variables via the modified Wheeler equation as follows:

$$V_b = \frac{W_e W_b}{C_0}\left[1 - \frac{1}{k_v \tau}\ln\left(\frac{C_0}{C_x}\right)\right] \qquad (2)$$

The term $W_e W_b / C_0$ represents the volume of air containing vapor at C_0 that would be required to reach thermodynamic equilibrium, V_t. Since the adsorption efficiency, $1 - \ln(C_0/C_x)\ /k_v\tau$, is generally ≤ 1, V_b is $\leq V_t$. The quantity $\ln(C_0/C_x)\ /k_v\tau$ represents the fractional unused bed capacity. The decrease in V_b as C_0 increases is partially offset by an increase in W_e with C_0, but since W_e typically exhibits a Langmuir, or similar, dependence on concentration, this compensation effect diminishes with increasing C_0.

The tradeoffs between Q, W_b, and τ can be considered in light of eq 2. Increasing Q leads to a proportional decrease in the instrument duty cycle (sampling duration), which is desirable. But this also leads to a decrease in τ and in the efficiency of adsorption, causing a decrease in V_b. For high Q values (approaching τ_c), the V_b increases sharply with Q. As Q is reduced, the bed becomes more efficient, and V_b becomes less dependent on Q, asymptotically approaching a limiting value corresponding to V_t. Increasing W_b at a specific value of Q leads to a proportional increase in τ and a similar approach of V_b to V_t. Applying eq 2 requires an initial series of measurements to establish W_e and k_v for a given adsorbent-vapor pair.[32] The effects of changes in W_b and Q (or τ) can then be determined.

Obviously, increasing the mass of adsorbent or decreasing the flow rate maximizes the breakthrough volume; however, increasing the adsorbent mass increases the pressure drop across the bed and may also increase the desorption bandwidth due to heat transfer limitations, increased dead volume, and residual adsorptive interactions of desorbing vapors as they are swept through the bed. Increasing the cross sectional area of the bed at constant W_b can reduce the pressure drop significantly (to a first approximation, pressure drop varies inversely with the sixth power of the bed radius for a constant adsorbent mass),[37] with no effect on τ or V_b. This, in turn, may allow a higher Q to be attained using a miniature pump. Increases in Q, however, will decrease V_b, as discussed above.

Slow heat transfer through the bed cross section may then become a limiting factor, but simply stopping the flow during the initial phase of the heating cycle should minimize band spreading from this factor. Backflushing reduces band spreading due to residual vapor-adsorbent interactions at high temperature. Under these operating conditions, the maximum bed depth is likely to be constrained by the mismatch between the bed cross section and that of the downstream channel. Interconnection through a reducing adapter to downstream components (e.g., the separation column), which are typically of capillary dimensions, can easily add significant dead volume. This dilutes the desorbed vapor and reduces the preconcentration factor.

EXPERIMENTAL METHODS

Materials. Testing was performed on 20 VOCs from seven different chemical classes that span a vapor pressure range from 8 to 231 Torr (Table 1).[38] All of the compounds were obtained from Aldrich (Milwaulkee, WI), Acros/Fisher (Pittsburgh, PA), or Lancaster (Windham, NH) at ≥99% purity. The following four vapors, which span the range of vapor pressures for the entire set of 20 compounds (Table 1), were used for initial tests of desorption and breakthrough: acetone, benzene, toluene, and *m*-xylene.

Table 2 lists the eight commercial adsorbent materials that were tested and some relevant physical properties. The porous polymers Tenax TA and Tenax GR were obtained from Alltech (Deerfield, IL); XUS43565.01 (20/50 mesh), which is a methylene-bridged copolymer of styrene and divinylbenzene abbreviated here as XUS565, was obtained from Supelco (Bellefonte, PA); the

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Table 2. Adsorbent Materials and Selected Physical Properties

adsorbent	type[a]	t_{max}, (°C)	t_{desorp}, (°C)	mesh	surface area, (m^2/g)	pore size, (Å)
XUS565	SDVB	180	160	20/50	1000	24
Carboxen 1000	CMS	<400	350	60/80	1200	10−12
Carbosieve SIII	CMS	<400	350	60/80	820	8−11
Carboxen 569	CMS	<400	350	20/45	485	5−8
Carbopack X	GC	<400	350	40/60	250	100
Carbopack B	GC	<400	350	60/80	100	N/A[b]
Tenax TA	DPO	350	300	35/60	35	2000
Tenax GR	DPO + GC	350	300	35/60	24	N/A

[a] SDVB: methylene bridged styrene divinylbenzene copolymer; CMS: carbon molecular sieve; GC: graphitized carbon; DPO: 2,6-diphenylene oxide porous polymer; [b]N/A: Not available

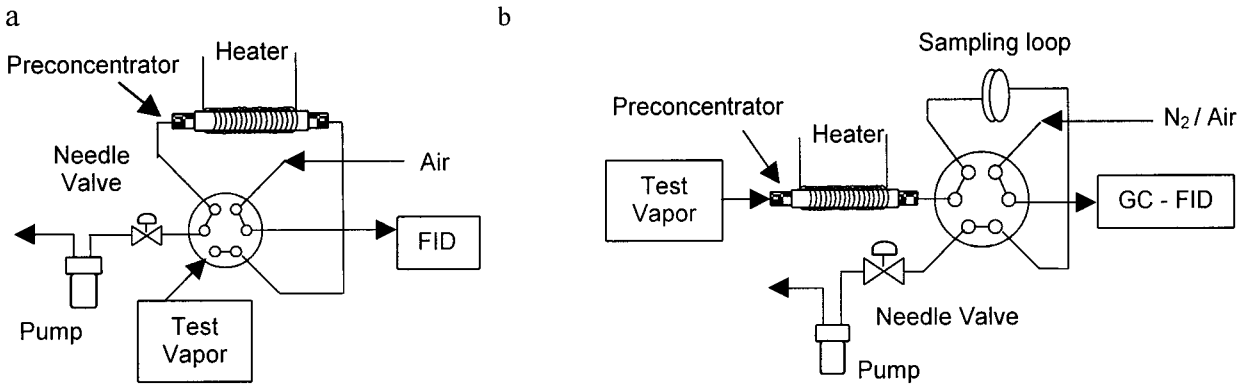

Figure 2. Configurations used for testing (a) desorption bandwidth and (b) breakthrough volume.

graphitized carbon blacks Carbotrap B and Carbopack X and the carbon molecular sieves Carbosieve SIII, Carboxen 1000, and Carboxen 569 were also obtained from Supelco.

Preconcentrator Construction. Preconcentrators were constructed from thin-walled glass capillaries (1.15-mm i.d., 1.70-mm o.d., Fisher) cut to a length of 7.5 cm. The mass of adsorbent packed into the tube ranged from 1 to 10 mg. Micromesh stainless steel screening was cut, folded, and inserted into each end of the capillary to retain the adsorbent. In subsequent tests, the preconcentrator adsorbents were packed in slightly larger bore stainless steel capillaries (1.32-mm i.d., 1.58-mm o.d.).

A fine-wire thermocouple was placed against the outer wall of the glass capillary and held snugly in place under a sleeve of polyimide (1.80-mm i.d., 0.051-mm wall, Cole Parmer; Vernon Hill, IL). A 55-cm section of Pt wire (0.13-mm diameter) with resistance of 0.1 Ω/cm was coiled around the polyimide tube to create a heated region that extended beyond that of the lengths of the adsorbent beds (bed lengths ranged from 0.24 to 0.54 cm/mg for the materials used). A PID controller (model 96A1, Wattlow; Winona, MN) and power supply (model DC1P, Wattlow) were used to control the heating profile for thermal desorption. The controller was adjusted to ramp from room temperature to the desorption set-point temperature (Table 2) within 3 s with less than a 15 °C overshoot in all cases.

Capillaries packed with the graphitized carbons, carbon molecular sieves, or porous polymers were preconditioned under N_2 at 270 °C for at least 4−12 h after initial packing and then at 300 °C for 10 min before use.[39−41] The XUS565 was heated to 160 °C under N_2 for 10 min before use.[16,21]

Test Atmosphere Generation. Test atmospheres were generated by injecting liquid solvent into a Tedlar bag prefilled with a known volume of clean, dry dilution air and then transferring aliquots into a series of additional bags. For testing humidity effects, dilution air was passed through a gas-sparging vessel containing distilled water prior to filling the Tedlar bag. An additional 50 μL of distilled water was injected into the bag to ensure saturation was maintained over the course of the experiments, since water vapor permeates rapidly through the bag wall.[42] The bags were at ambient temperature (26 ±2 °C) over the course of testing.

Desorption Efficiency. Figure 2a shows the experimental setup used for testing the desorption characteristics of the various adsorbents. The preconcentrator assembly was connected via deactivated fused-silica capillary tubing (0.25-mm i.d.) to a six-port, zero-dead-volume valve (HP5062-9508, Agilent Technologies; Wilmington, DE) installed in a thermostated chamber mounted on the GC chassis. Valve sequencing and data acquisition were controlled from a personal computer running ChemStation software (Agilent Technologies).

For desorption bandwidth determinations, 10 mg of each adsorbent was packed into the glass capillary. A 1-L sample of vapor at 0.5 ppm was drawn through the preconcentrator (0.1 L/min) using a small diaphragm pump. The flow through the capillary was then stopped and the heater was activated. Upon reaching the set-point temperature (<3 s), the six-port valve was actuated, and the sample was backflushed to the FID on a background of clean, dry air at a flow rate of 4 mL/min. Heating was continued for 30 s.

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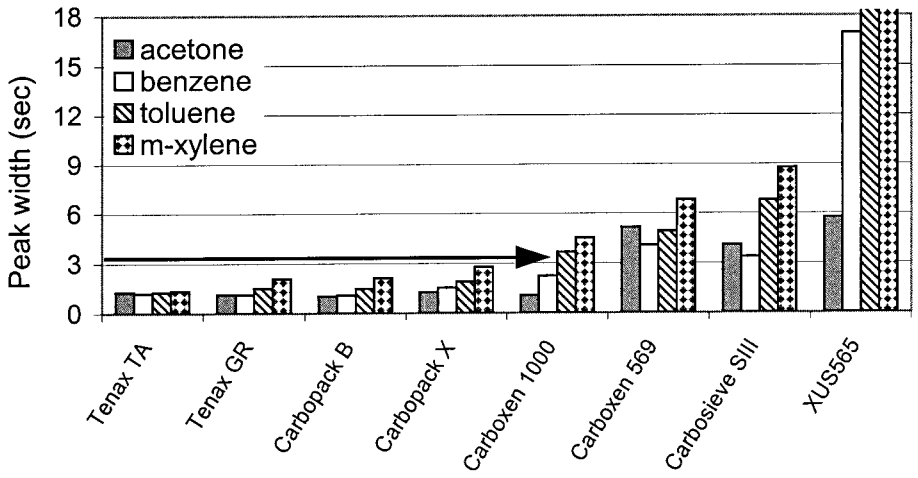

Figure 3. Desorption half-height peak widths for four vapors (10 mg of each adsorbent, 4 mL/min desorption flow rate, dry-air matrix).

Breakthrough Volume. Figure 2b shows the setup used for determining breakthrough volumes. Vapor samples at 0.1 or 1 ppm in air were drawn through the preconcentrator and through a downstream 250-μL sampling loop at 0.1 L/min. At 1-min intervals, the six-port valve was actuated to inject the sampling loop volume into the GC-FID using an N_2 carrier gas. The breakthrough volume was defined as the sample volume required for the vapor concentration downstream from the preconcentrator to reach 10% of inlet concentration (i.e., $C_0/C_x = 10$). Peak height was used for quantification, and breakthrough volumes (times) were determined to the nearest 0.05 L (0.5 min) by linear interpolation where necessary. For these tests, the GC was equipped with a 30-m capillary column (250-μm i.d.) having a 0.25-μm poly(dimethylsiloxane) stationary phase layer (HP-1, Agilent Technologies).

SAW Sensor Array. The sensor array was designed and constructed by researchers at Sandia National Laboratories and consists of four SAW delay lines having a common launching transducer and four receiving transducers, all of which integrated on a single ST-quartz substrate.[13,14,43] Each device has an active area of ~0.24 mm^2, and the entire array occupies an area of <3 mm^2. Signal processing electronics are situated directly on the quartz substrate and a Pyrex cover plate sealed over the assembly produces a detector cell with a dead volume of ~1 μL. Capillaries emanating from holes etched in the coverplate provide for gas flow over the array and are anchored in place with epoxy.

The nominal operating frequency of each sensor is 520 MHz, as determined by the spacings of the interdigital transducer electrode finger-pairs (i.e., 6 μm); however, the sensors were not operated as oscillators. Rather, the phase delay was measured by an in-phase and quadrature method that permits output measurements in dc voltage rather than in frequency. Output signals were monitored via an A/D interface board on a personal computer. Details of device design and operation can be found elsewhere.[43,44] For the test results reported here, only one of the four sensors in the array was monitored. This sensor was coated with a thin layer of a polymer referred to as BSP3, which is a poly(dimethylsiloxane) having hexafluorobisphenol A moieties incorporated along the backbone,[45,46] graciously provided by Dr. Jay Grate of Pacific Northwest National Laboratories. The sensor array was operated at ambient temperature.

RESULT AND DISCUSSION

Desorption Bandwidth. The desorption bandwidth will vary with the desorption temperature, flow rate, vapor volatility, and vapor-adsorbent affinity. For initial screening experiments of all the adsorbents, the desorption temperature was set 20−50 °C below the maximum recommended operating temperature provided by the adsorbent manufacturer (Table 2). The air flow was stopped for 3 s during initiation of the preconcentrator heater on the basis of preliminary tests with *m*-xylene, which indicated narrower and more reproducible desorption profiles than with continuous flow. The desorption flow rate of 4 mL/min is typical of those used for capillary GC separations and was achievable using a small diaphragm pump, even with a 12-m length of capillary column in-line.[11] A desorption bandwidth ≤ 3 s was sought in order to achieve a minimum preconcentration factor of ~5×10^3 for a 1-L sample volume desorbed into a flow of 4 mL/min. Given the expected range of sensitivities for the SAW sensor,[16] this would allow detection limits in the low-parts-per-billion range for most vapors.

Figure 3 presents the desorption bandwidths obtained from each adsorbent for each of the four test vapors. Tenax TA, Tenax GR, Carbopack B, and Carbopack X provided very sharp desorption peaks for all four test vapors. Previous work in our laboratory had shown XUS565 to be a useful single-adsorbent preconcentrator with a large capacity for a wide range of vapors and low-water-vapor affinity.[16,21] As shown in Figure 3, however, its slow desorption, particularly for the less volatile members of the vapor test set, argues against its use for this application. This behavior can be attributed to a combination of the low maximum temperature (160 °C) and high surface area of the XUS565.

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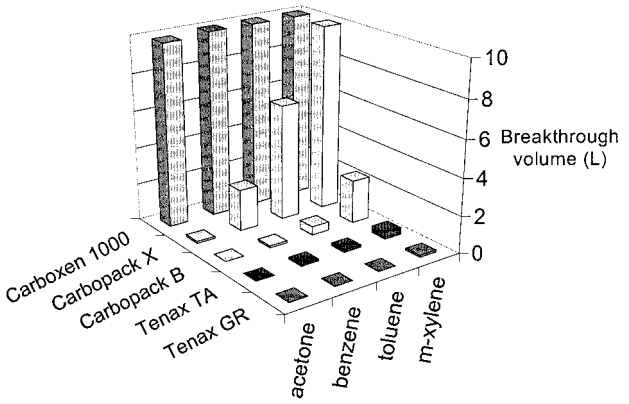

Figure 4. Individual vapor breakthrough volumes (10%) for vapor concentrations of 1 ppm and adsorbent masses of 5 mg.

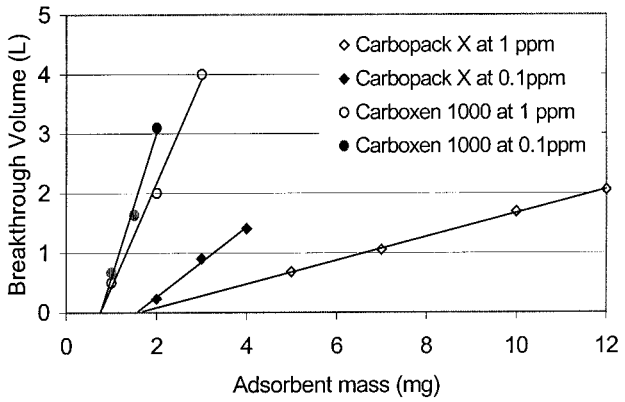

Figure 5. Breakthrough volume (10%) as a function of the adsorbent mass and vapor concentration for the 20-vapor mixture using benzene as the breakthrough indicator vapor for Carbopack X and for the seven-vapor mixture using acetone/2-propanol as the indicator compounds for Carboxen 1000.

Among the carbon molecular sieves, Carbosieve SIII and Carboxen 569 gave similar, relatively broad desorption peaks for all four vapors. This was expected for the less volatile toluene and *m*-xylene but not for acetone or benzene.[47] The consistently sharper bandwidths observed with the Carboxen 1000 are surprising, given its higher surface area. Apparently, among these carbon molecular sieves, the larger average pore size of the Carboxen 1000 allows more efficient VOC desorption.

Breakthrough Volumes. Having eliminated XUS565, Carbosieve SIII, and Carbosieve 569 on the basis of desorption bandwidth, the remaining adsorbents were tested for their adsorption capacity using beds containing 5 mg of each adsorbent and a challenge concentration of 1 ppm of each vapor (individual exposures to each vapor). The 10% breakthrough volumes in Figure 4 show that Tenax TA and Tenax GR lack sufficient capacity, because $V_b \ll 1$ L in all cases. Carbopack B performed adequately only for *m*-xylene, Carbopack X provided adequate capacity for all of the vapors except acetone, and Carboxen 1000 provided excellent capacity ($V_b > 10$ L) for all of the vapors.

Taken together, the results of desorption and breakthrough tests suggest that a bed packed with Carbopack X and Carboxen 1000 would provide the best overall performance. The expectation was that benzene and compounds less volatile than benzene would be trapped on the Carbopack X bed, and those more volatile than benzene would be distributed between the two beds but trapped predominantly on the downstream Carboxen 1000 bed.

Benzene was designated as the "cutoff" vapor for the Carbopack X, and breakthrough tests were performed using the 20-vapor test set, each vapor at 1 ppm, with a 10-mg bed of this adsorbent material. As expected, the seven compounds less volatile than benzene gave smaller breakthrough volumes: acetone, 2-propanol, dichloroethane, methyl ethyl ketone, ethyl acetate, 2-methylfuran, and 1,1,1-trichloroethane. The breakthrough volume for trichloroethylene on Carbopack X was nearly identical to that of benzene. The breakthrough order varies inversely with vapor pressure with the exception of 2-propanol, which coelutes with acetone, despite its lower vapor pressure. This follows from the nonpolar nature of the Carbopack X. Benzene and all of the vapors less volatile than benzene gave larger breakthrough volumes (i.e., >1.7 L).

Similar tests performed on a 2-mg bed of Carboxen 1000 using a mixture of the seven vapors with breakthrough volumes smaller than that of benzene on Carbopack X (each vapor at 1 ppm) revealed that acetone and 2-propanol are the first to breakthrough the adsorbent bed and that they coelute. Therefore, this pair of vapors was selected for determining the required mass of Carboxen 1000 in the dual bed.

Figure 5 shows the dependence of the breakthrough volume on the adsorbent bed mass for Carbopack X and Carboxen 1000 at each of two challenge concentrations. The Carbopack X was challenged using the 20-vapor mixture at component concentrations of 100 ppb and 1 ppm. The benzene breakthrough volume varies roughly linearly with increasing bed mass at both concentrations. At 100 ppb, a mass of 3.4 mg is required to maintain a breakthrough volume ≥1 L for the 13 least volatile vapors in the test set, but at 1 ppm, the required mass increases to 7.0 mg. Thus, a 10-fold increase in concentration requires only a ~2-fold increase in bed mass, reflecting the increase in W_e with C_0 and the increase in V_t and τ with W_b (cf. eq 2). Similarly, Carboxen 1000 was challenged using the subset of seven vapors shown to break through the Carbopack X prior to benzene, using acetone/2-propanol as the indicator vapors. The breakthrough volume increases linearly with bed mass, and 1.2 and 1.5 mg are required to maintain a breakthrough volume ≥1L for challenges of 100 ppb and 1 ppm, respectively.

The Carbopack X and Carboxen 1000 were then tested at 100% humidity with the same mixtures (20 vapors for the Carbopack X and 7 vapors for the Carboxen 1000). There was no significant effect on the retention of vapors on the Carbopack X. Breakthrough volumes for benzene and the seven vapors with smaller breakthrough volumes were within ±4% of those determined at 0% RH, and no breakthrough was observed for the less volatile vapors at the higher RH up to a sampling volume of 1.7 L. The Carboxen 1000, however, showed a significantly lower breakthrough volume for acetone/2-propanol at high humidity. The affinity of Carboxen 1000 for water vapor is well-known, and some decrease in capacity for the target vapors was expected.[48] Testing using different masses of Carboxen 1000 against the seven-vapor mixture at 0 and 100% RH gave the results shown in Figure 6. Increasing the Carboxen 1000 bed mass from 1.2 mg, which was

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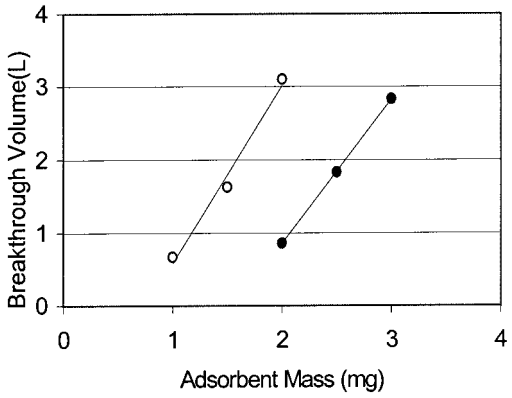

Figure 6. Breakthrough volume (10%) as a function of Carboxen 1000 adsorbent mass for the seven-vapor mixture at 100 ppb using acetone/2-propanol as the breakthrough indicator compounds (open symbols: 0% RH; filled symbols: 100% RH).

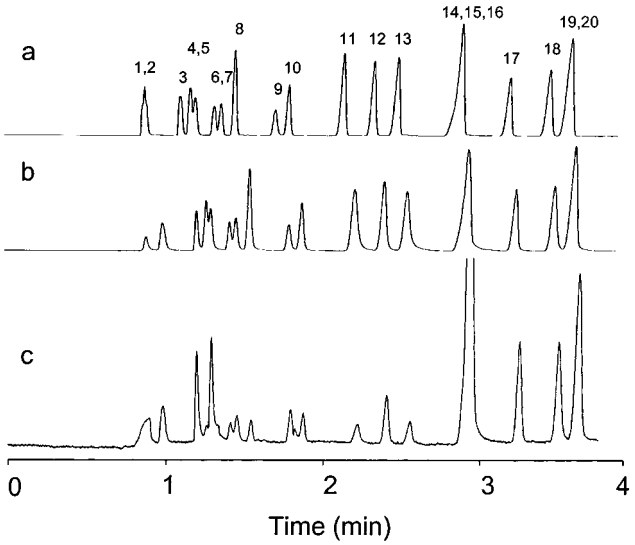

Figure 7. 20-vapor chromatograms for (a) 0.1-mL injection loop; (b) preconcentrator injection with FID; (c) preconcentrator injection with SAW detector (*y*-axis scale increased 3×). GC conditions: 4 mL/min; 35 °C for 1 min then 15 °C/min ramp to 80 °C. See Table 1 for peak identifications.

adequate to trap these vapors at 100 ppb at 0% RH, to 2.1 mg at 100% RH increased the breakthrough volume to an acceptable level. It should be noted that these are considered worst-case exposure conditions for the Carboxen 1000, since some fraction of the more volatile vapors will be retained on the Carbopack X, and the likelihood of encountering indoor working environments at 100% RH is low.

Microsensor System Performance. Tests were continued using the dual-bed preconcentrator containing 3.4 mg of Carbopack X and 2.1 mg of Carboxen 1000. Reducing the desorption temperature from 350 to 300 °C did not affect the desorption bandwidth; therefore, subsequent tests employed this desorption temperature, which provided a half-height peak width of 2.7 s for the 20-vapor mixture when desorbed directly into the FID at 4 mL/min. This corresponds to a preconcentration factor of ~5500. Desorption efficiencies were examined by analyzing a 1-L blank dry-air sample directly after analysis of a 1-L 20-vapor sample (100 ppb). For most of the vapors, there was no detectable vapor in the blank sample, and in all cases, the residual vapors were present at <1% of the initially measured level.

Figure 7a,b compares chromatograms obtained using the preconcentrator to those obtained with a standard 0.1-mL sampling loop under identical analytical conditions. Vapor concentrations were adjusted so that the injected mass was equivalent to a 1-L sample at 100 ppb in all cases. As shown, the peak shapes and resolution are virtually identical in the two cases. This confirms that the desorption bandwidth achieved with the preconcentrator does not degrade chromatographic efficiency. The shift in retention times for the preconcentrated sample is attributed to a short section of passivated capillary tubing required for connection to the GC column and some residual dead volume in the preconcentrator itself. The sampling loop was mounted directly on the GC chassis with a much shorter connection line.

Figure 7c shows a chromatogram obtained with the preconcentrator using the SAW sensor as the detector. The finite rates of vapor sorption/desorption in the polymeric sensor coating cause slight peak broadening and some loss of resolution. Differences in the relative sensitivities as compared to the FID arise from differential degrees of vapor/polymer partitioning; however, peak shapes and resolution are still adequate. The first peak in Figure 7b,c is an artifact, apparently arising from decomposition of certain of the oxygenated vapors in the vapor test set. Although the identity of this compound was not determined, it is almost unretained on the column and does not interfere with the analysis of the target analytes.

As stated above, the sample volume of 1 L was chosen in anticipation of achieving a certain preconcentration factor and a certain range of LODs from the SAW sensor(s). Table 1 shows that the LODs obtained from the SAW sensor, although higher than those from the FID, are in the desired low-parts-per-billion range.

Medium-term aging tests were performed on a 5-mg bed of Carbopack X challenged using a trichloroethylene/toluene mixture (500 ppb) and a separate 2-mg bed of Carboxen 1000 challenged using an acetone/2-methylfuran mixture (500 ppb). A total of 200 samples (1 L) of each mixture in dry N_2 were collected and then desorbed at 300 °C directly into the GC-FID. The breakthrough volume was determined initially and then after every 50 cycles. Neither adsorbent showed any signs of aging (peak shape, retention time, and breakthrough volume), and there was no evidence of artifact formation.

Design and Performance Modeling. Over the range of flow rates tested (i.e., 0.075−0.4 L/min), the pressure drop increased linearly with flow rate for both the glass and stainless steel preconcentrator tubes. The ratio of the slopes of the pressure-flow relationships was 2.75 (glass:stainless steel) for the same adsorbent mass. Given that the stainless steel tube diameter was 18% larger, the theoretical pressure drop ratio was expected to be 2.7.[37] Thus, agreement between experiment and theory is quite good. For a dual-adsorbent bed packed with 7 mg of Carbopack X and 2 mg of Carboxen 1000, the maximum flow rate achievable with the miniature diaphragm pump to be used in the final instrument was 0.256 L/min with the glass tube, increasing to 0.477 L/min for the wider bore stainless steel tube. Desorption peak widths were equivalent with both tubes; thus, the stainless steel tube appears to provide more flexibility in sampling rate.

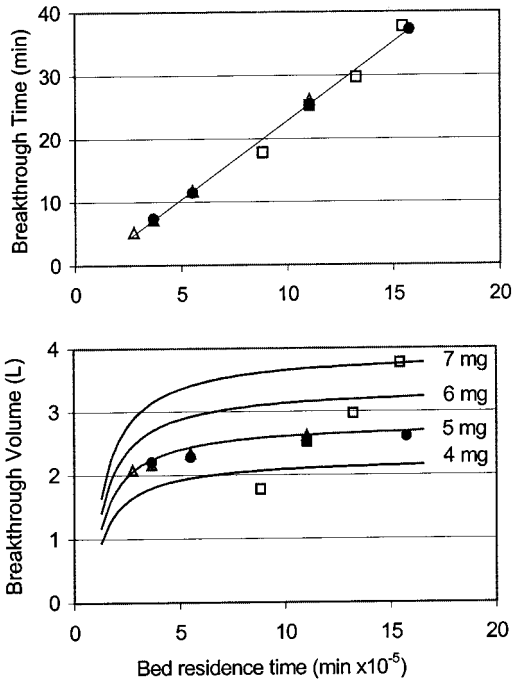

Figure 8. Modeled and experimental breakthrough parameters for 1 ppm of benzene and Carbopack X: (a, top) breakthrough time vs bed residence time (b, bottom). Breakthrough volume vs bed residence time: ●, 5 mg in glass tube; □, 4−7 mg in glass tube; △, 5 mg in stainless steel tube; −, modified Wheeler model.

According to eq 1, the breakthrough time is inversely proportional to the bed residence time. Figure 8a shows the effect of the bed residence time on the breakthrough time (10%) with the glass and stainless steel preconcentrator tubes for benzene adsorption on Carbopack X. Tests were performed over a range of different flow rates and adsorbent masses at a challenge concentration of 100 ppb. All of the data fall along the same line, which is consistent with expectations. The critical bed residence time is 8.2×10^{-6} min (0.49 ms). At a flow rate of 0.1 L/min, this corresponds to a critical bed mass of 1.82 mg and for the stainless steel tube, a critical bed length of 0.30 cm. Values of 0.0018 g/g for W_e and 266160 min^{-1} for k_v were obtained by regression from the slope and intercept, respectively, of the line in Figure 8a.

Figure 8b presents a series of curves derived from eq 2 that show the predicted relationship between the breakthrough volume and the bed residence time for benzene on Carbopack X, based on the estimates of W_e and k_v derived from Figure 8a. Data collected using 5-mg beds of Carbopack X in the glass and stainless steel tubes at different flow rates show similar fits to the model. Modeled curves for bed masses of 4, 6, and 7 mg are also presented, along with independent experimental data (open squares) for each bed mass. Table 3 summarizes these data and provides estimates of the bed efficiency for each test condition. The model tends to overestimate the breakthrough volume somewhat, but in all cases, the error is within ±18%. The fact that the error increases with decreasing bed mass suggests that the estimate of k_v from Figure 8a may be slightly low, because errors in k_v will have a larger effect on predicted breakthrough volumes for smaller bed masses.

When the bed residence time is relatively long, the breakthrough volume is nearly independent of the bed residence time (or flow rate). As the critical bed residence time is approached, there is sharp decline in the breakthrough volume. If the flow rate at which one desires to operate results in too low a bed residence time, then additional mass must be added to account for the reduction in breakthrough volume. For example, for a starting mass of 5 mg and a flow rate of 0.1 L/min through the glass capillary, the bed residence time is 1.1×10^{-4} min, the bed efficiency is 92%, and the breakthrough volume is 2.54 L. If the same mass of Carbopack X is packed into the stainless steel tube and the flow rate is increased to 0.4 L/min (e.g., to reduce the instrument duty cycle), the bed residence time is reduced to 2.8×10^{-5} min, the efficiency is reduced to 69%, and the breakthrough volume decreases to 2.08 L. To regain the original breakthrough volume requires a compensation mass of 1.05 mg of added adsorbent, according to the model (eq 2). The 21% increase in adsorbent mass (W_b) leads to commensurate fractional increases in V_t and τ. This 21% increase in τ corresponds to an increase in bed efficiency of only 5%, from 69% to 74%. Thus, operating at high flow rates leads to inevitable decreases in the efficiency of adsorption that can only be compensated for by increasing the capacity through an increase in adsorbent mass. The modified Wheeler model permits precise estimates of the minimum mass required to maintain the required breakthrough volume. In this example, a 4-fold decrease in sampling time was possible by adding only 21% more adsorbent to the preconcentrator.

Table 3. Modeled and Experimental Data for Benzene Preconcentration on Carbopack X

mass (mg)	Q (L/min)	τ (min $\times 10^{-5}$)	efficiency[a] (%)	breakthrough vol L		error (%)
				modeled[b]	exptl	
5	0.070	15.8	94.5	2.67	2.60	+2.4
5	0.100	11.0	92.2	2.60	2.54	+2.4
5	0.200	5.52	84.3	2.38	2.28	+4.3
5	0.300	3.68	76.5	2.16	2.20	−1.9
5	0.400	2.76	68.6	1.94	2.08	−6.9
4	0.100	8.83	90.2	2.04	1.78	+18
5	0.100	11.0	92.2	2.60	2.52	+3.2
6	0.100	13.2	93.5	3.16	2.93	+8.0
7	0.100	15.5	94.4	3.73	3.77	−1.1

[a] Bed efficiency = $[1 - (1/k_v\tau)\ \ln(C_0/C_x)]$ [b] Modified Wheeler model (eq 2) with $W_e = 0.0018$ (g/g) and $k_V = 266158$ (min^{-1}) from Figure 8a.

CONCLUSIONS

This study has illustrated that with proper design, the tradeoff between adsorption capacity and desorption bandwidth required for combining sampling and focusing functions within a thermally desorbed vapor preconcentrator can be accommodated without sacrificing overall performance. A complex 20-vapor mixture spanning a vapor pressure range of 2 orders of magnitude can be quantitatively trapped at the 100 ppb level and efficiently thermally desorbed using a preconcentrator containing <6 mg of judiciously selected adsorbent materials. The narrow preconcentrator injection bandwidth that is achieved permits efficient chromatographic separation and low-parts-per-billion detection limits with a surface

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acoustic-wave sensor from a 1-L volume of sampled air. The performance thus appears adequate for indoor air quality assessments for VOCs.

Integral to the experimental design employed here was a detailed examination of the distribution of vapors between the adsorbent materials considered for inclusion in the preconcentrator. This permitted precise determinations of the types and amounts of adsorbents that were required to achieve the minimum required composite breakthrough volume, while also maintaining the desired limit on the desorption bandwidth.

The modified Wheeler model provides a useful framework for considering the effects of various design and operating options on the bed residence times and consequent breakthrough volumes. Strictly speaking, this model is applicable only to a single vapor, because W_e and k_v are vapor-specific. However, it could be applied to mixtures of vapors by selecting an "indicator vapor" from among the mixture components and determining the effective values of W_e and k_v for that vapor.[49] Performance variations then could be assessed under limiting conditions, such as the maximum number of anticipated mixture components at the highest possible concentrations and humidity level.

Extension of this development effort to include semivolatile vapors is currently underway and is being implemented using the approaches and concepts described here. This will permit the near-real-time analysis of a wider range of indoor air contaminants.

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