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Evaluating porous-layer open-tubular capillaries as vapor preconcentrators in a microanalytical system

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Abstract

Measuring environmental concentrations of organic vapors with microfabricated chemical sensors or sensor arrays often requires a means to enrich collected samples prior to detection. With such an application in mind, a preliminary evaluation is described of two porous-layer open tubular (PLOT) capillary traps as vapor preconcentrators for a series of vapors. Short (1-cm) sections of commercial PLOT-Q and PLOT-S capillary having wall coatings of styrene–divinylbenzene copolymer and vinylpyridine–divinylbenzene copolymer, respectively, are fitted with a metal sleeve for rapid thermal desorption of preconcentrated vapor samples, and tested using a downstream 97-MHz polyisobutylene-coated surface acoustic wave (SAW) sensor. Calibrated responses to vapors of 2-butanone (MEK), trichloroethylene (TCE), toluene, and *m*-xylene are collected with and without preconcentration. Dimethylmethylphosphonate could not be efficiently desorbed from either PLOT trap. For the remaining vapors, increases in sensitivity of 3–9-fold are achieved by preconcentrating and analyzing just 1 ml of sample air. Calculated limits of detection (LOD) range from 1–8 ppm. Differences in sensitivities are observed between the PLOT-Q and PLOT-S sampling trains for MEK and TCE. A theoretical model of penetration yields limiting values of flow rate and trap dimensions. Measured 10%-breakthrough times at 1 ml/min ranged from ~1 to 6 min and, for PLOT-Q, are ≥ modeled values obtained using the modified Wheeler equation. The implications of the results for the design and operation of microanalytical systems for vapor analytes are discussed.

Keywords: Microanalytical system; PLOT; Preconcentrator; Surface acoustic wave sensor; Vapor sensor

1. Introduction

Recent reports on microfabricated sensor arrays for analyzing gases and vapors have shown that recognition and discrimination of multiple organic vapors is possible using any of several different sensing platforms [1–10]. It is becoming increasingly clear, however, that the development of practical microsensor-based instrumentation will rely on coupling the sensing elements with ancillary components in so-called microanalytical systems. For many environmental and occupational health monitoring applications, for example, the limited sensitivities of most available microsensors for volatile organic compounds demand some sort of enrichment stage prior to analysis in order to bring minimum detection levels within the range of regulatory concentration limits.

Prototype instruments equipped with small thermally desorbed preconcentrators coupled to microsensors or microsensor arrays have been described [11–16]. Typical designs comprise a thin-walled glass or metal tube, 1–5 mm in diameter, packed with a granular porous polymer and wrapped with a resistive heater coil. The role of the preconcentrator is threefold: it focuses the sampled vapors by collecting them from a large volume of air and desorbing them into a smaller volume of air; it provides some immunity from baseline drift since the sensor response from a desorbed pulse of vapor is generally rapid relative the time scale of drift; and it can reduce the amount of water vapor in desorbed samples by use of hydrophobic adsorbents [11,15]. It has also been shown that elution times of desorbed peaks can vary and that this can be used to enhance vapor recognition and discrimination [5,6, 12,14,16].

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Pressure drops can be significant across such tubes, particularly if smaller particles are used [11], and reproducibly packing/retaining the adsorbent in the tube via glass wool or finewire screening can be tricky. If the volume of the adsorbent bed is large relative to the interconnecting tubing and/or the detector cell, dilution and peak-broadening may be excessive and heating power requirements increase. Duty cycles also may be limited by the additional time required for cooling prior to subsequent sample collection [5,12]. All of these factors argue for reducing the size of the preconcentrator. However, with size reductions come tradeoffs in sample capacity, flow rate, and other factors affecting system performance.

The use of wall-coated open-tubular capillaries having sub-millimeter diameters as alternatives to more conventional packed-bed preconcentrators would address some of the shortcomings of the latter in the construction of microanalytical systems for organic vapors. Porous-layer open-tubular (PLOT) capillaries having inner diameters of 250–530 μm are commercially available with a range of different porous–polymer wall coatings. Although vapor collectors configured from capillaries coated with thick stationary-phase films and/or pulverized granular adsorbents have been reported for gas chromatographic headspace analysis [17–21], such studies have been limited in scope, and general design and operating parameters relevant to microanalytical systems for organic vapors have not been addressed.

In this study, a preliminary investigation of short sections of PLOT capillaries as thermally desorbable vapor preconcentrators was performed using a polymer-coated surface acoustic wave (SAW) oscillator, enclosed within a microchannel, as the detector. Five organic vapors and two commercial wall-coated PLOT traps were tested. Response profiles, sensitivity enhancement factors, and 10% breakthrough times were determined for each type of PLOT preconcentrator and the effect of trap length was examined. Models of vapor penetration and adsorption capacity were applied to these structures and experimental breakthrough times were compared to modeled values for one of the PLOT traps.

1.1. Models of penetration and breakthrough time

To capture vapors efficiently within a PLOT capillary, the residence time of the vapors must be sufficient to ensure collision of the vapor molecules with the coated wall and the adsorption capacity must be sufficient to avoid breakthrough losses over the required range of vapor concentrations and sample volumes.

The first issue can be assessed in terms of the fractional penetration, P, of vapor passing through the capillary. For a channel of circular cross-section having an adsorptive wall, the minimum length, L, required to ensure contact of the vapor molecules with the wall can be determined as a function of volumetric flow rate, Q, and vapor diffusion coefficient in air, D, from a well-established theory that has been applied successfully to the construction of cylindrical aerosol denuders [22,23]:

$$P = 0.819\mathrm{e}^{-3.66\mu} \tag{1}$$

where $\mu = DL\pi/Q$ is a dimensionless parameter. It is assumed in this model that the vapor concentration is fixed, flow in the tube is laminar, vapor diffusion in the direction of flow is negligible, and the sticking coefficient of the vapor on the wall is unity. Analogous expressions are known for other cross-sections (e.g., rectangular). This model can specify initial constraints on L and Q for preconcentrating vapors within a specified range of D values.

The adsorption capacity of the porous polymer within the PLOT capillary at a given temperature will vary with the vapor concentration and the inherent affinity of the polymer adsorbent layer for the vapor. Under a given set of conditions, the point at which vapor breaks through a trap of specific length (adsorbent mass) can be expressed in terms of the breakthrough volume or the breakthrough time, t_B. The following modification of the Wheeler Model has been used successfully to describe the dependence of t_B on several operating variables for organic vapors drawn through packed beds of granular adsorbents [11,24–29]:

$$t_\mathrm{B} = \frac{W_\mathrm{e}}{C_0 Q}\left[W - \frac{\rho_\mathrm{b} Q}{K_\mathrm{v}}\ln\left(\frac{C_0 - C}{C}\right)\right] \tag{2}$$

where W_e is the adsorption capacity (mg/g), C_0 is the inlet vapor concentration (mg/ml), C is the vapor concentration downstream from the bed (mg/ml), Q is the volumetric flow rate (ml/min), W is the weight of adsorbent (g), ρ_b is the bulk density of packed bed (g/ml), and K_v is the rate constant (min^{-1}). Eq. (2) predicts the time (minutes) required for C to reach some fraction of C_0. Values for C_0, W, Q, and ρ_b are typically known, leaving K_v and W_e to be determined. If estimates of K_v and W_e are already available, then t_B can be predicted directly.

In a previous study in our laboratory, values of K_v and W_e were determined for 2-butanone (MEK), trichloroethylene (TCE), xylene and other vapors trapped on a packed bed of a highly porous styrene–divinylbenzene resin of nominally similar structure to that used in the PLOT-Q capillaries examined in this study [11]. W_e varied with concentration, asymptotically approaching a limiting value in accordance with a Langmuir adsorption model. In addition, at a given vapor concentration, W_e varied inversely with vapor pressure among the five compounds tested.

Data from that study were combined here to derive the following expression for W_e as a combined function of vapor pressure and vapor concentration:

$$W_\mathrm{e} = C\mathrm{e}^{-0.014 p_\mathrm{v}} \tag{3}$$

where C is the vapor concentration in units of ppm and p_v is the vapor pressure in torr. This expression allows W_e values to be estimated as a function of concentration for untested vapors. However, the model is only approximate: while at vapor concentrations ≤ 100 ppm errors in modeled W_e values were generally $<16\%$ for the vapors used to establish the model, at higher concentrations errors ranged from 8% to 38%. Errors in W_e result in proportional errors in t_B using Eq. (2). Nevertheless, the overall accuracy of Eq. (3) was considered high enough for estimating W_e for the one previously untested vapor examined in the current study, toluene.

Values of K_v from the previous study did not show any trends that permitted a general model to be constructed, though K_v did increase with increasing molecular weight for the structural homologues acetone and MEK. K_v is known to vary with linear velocity, and the size, shape, and density of adsorbent granules [28]. Since the linear velocities and adsorbent-bed densities were very similar between the current and previous studies, K_v values from the previous study were used directly for the three vapors common to both studies: *m*-xylene, MEK, and TCE. K_v values for toluene were extrapolated from those of *m*-xylene by multiplying the latter by the molecular weight ratio of the two vapors. The dependence of t_B on K_v is relatively weak for the low fractional breakthrough concentrations of concern here, so small errors in K_v estimates can be tolerated without affecting t_B predictions seriously.

Use of these approaches to estimating W_e and K_v values for the current study assumes that the adsorptive strengths of the polymer resin and the PLOT polymer layer are similar. Another assumption is that Eq. (2), which was derived for packed beds, can be applied to a PLOT capillary having only a thin wall coating of adsorbent polymer merely by adjusting the bed packing density term.

2. Experimental

2.1. Materials

Table 1 lists the five solvent vapors tested along with several relevant physical properties. Toluene, *m*-xylene, TCE, MEK, and dimethylmethylphosphonate (DMMP) were purchased from Aldrich (Milwaukee, WI) in $>97\%$ purity and used as received. The silanizing agent, dimethyldichlorosilane (DMDCS), was obtained from Supelco (Bellefonte, PA) as a 5% solution in toluene. Polyisobutylene (PIB), used as the SAW sensor interfacial coating, was also obtained from Aldrich. A 15-m long, 0.250 mm i.d. fused silica capillary column having a wall coating of styrene divinylbenzene (PLOT-Q, Chrompack, Raritan, NJ) and a 30-m long, 0.320 mm i.d. capillary column having a wall coating of vinylpyridine–divinylbenzene copolymer (PLOT-S, Chrompack) were used to fashion the preconcentrators (note: the PLOT-S capillary was not available in the narrower bore). Passivated fused-silica capillary (0.250 mm i.d.) sections and standard glass capillary connectors served to connect the system components.

2.2. Detector design

The detector used in this study consists of an array of four 97-MHz SAW delay lines patterned end-to-end on a single ST-quartz substrate. Each SAW device has two symmetric Au-on-Cr interdigital transducers (IDT) consisting of 50 electrode pairs with an acoustic aperture of 1.6 mm, a center-to-center spacing of 7.25 mm and an overall active area of 11.6 mm^2 [33]. The array was epoxied to a brass plate and then glued into the center of a custom PC board with a cut-out section designed to accept the array strip. The input and output transducers on each device were wire bonded to surface-mounted series inductors and the other side of each transducer was connected to electrical ground. Coaxial SMB connectors mounted to the underside of the PC board were used for signal transmission. Each of the four SAW sensors was operated as an oscillator (see below) and spray-coated with PIB from toluene solution. The amount of PIB applied was that corresponding to a frequency shift of 200–250 kHz.

A Pyrex glass cover channel with a recess etch (40 μm deep × 1.8 mm wide) along its length was bonded to the quartz sensor-array substrate using UV-curable glue by exposure to a long-UV lamp and heating to 100°C. Inlet and outlet holes (~1 mm in diameter) were electrochemically drilled at each end of the cover channel prior to mounting. Rubber septa (Thermogreen LB-2, Supelco) were placed over the inlet and outlet holes, secured with a silicone sealant, and pierced with 10-cm sections of passi-

Table 1
Physical properties of the test vapors [22,30–32]

Chemical	Density^a (g/cm^3)	p_v^a (torr)	Boiling point (°C)	D (cm^2/s)	W_e^b (mg/g)	K_v^b (min^{-1})
MEK	0.805	94	79	0.0903	43	28 000
TCE	1.465	73	87	0.0875	58	15 000
Toluene	0.865	22	111	0.0849	103	27 000
m-Xylene	0.864	8	139	0.0670	107	31 000
DMMP	1.145	1	181	0.0817	–	–

^{a}At 25°C.
^{b}Evaluated at the concentrations specified in Table 2.

vated capillary to permit connection of the detector assembly to the rest of the system.

During the course of cover channel mounting, the two innermost SAW devices were rendered non-functional. Following initial testing, the downstream device became less stable, so experiments were performed using only the fourth (furthest upstream) SAW sensor. The sensor was operated as the frequency controlling element in a feedback oscillator circuit using a dual-stage rf amplifier (Model 8447D, Hewlett Packard, Palo Alto, CA). The output frequency was monitored at a rate of 1 Hz with a digital frequency counter (Model 53181A, Hewlett Packard) and transferred via an IEEE-4888 interface to a personal computer using BenchLink Meter software (Hewlett Packard).

2.3. Test system

Fig. 1 shows the test-system layout. A glass y-connector at the system inlet was used to switch between two different test atmospheres without opening the system. Each branch of the y-connector was fitted with a manual Teflon® on–off valve and a short extension piece of passivated capillary. Test atmospheres were generated in Tedlar® bags at a given concentration and then connected to the system via a septum on the bag. All test atmospheres were analyzed by GC/FID.

The downstream side of the y-connector accepted one end of a 6-cm section of PLOT capillary whose ends had been carefully scraped clean of the polymer wall coating using a fine wire to leave a 1.0- or 1.5-cm center section with the porous polymer still intact. Microscopic inspection of the preconcentrator confirmed removal of the wall coating from all but the center section. The downstream end of the PLOT capillary was inserted into a glass capillary connector packed with two small plugs of glass wool to prevent any loose wall coating from passing to the detector. Early trials revealed that this could be a problem and that the entire 1-cm plug of wall-coated section could actually shift if enough of a pressure differential was applied across the preconcentrator. The downstream side of this connector accepted the capillary section from the detector-assembly inlet. The total dead volume from the inlet port to the first sensor in the detector assembly was approximately 8 μl.

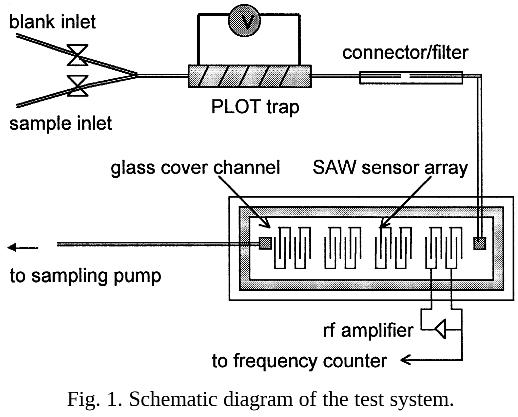

Fig. 1. Schematic diagram of the test system.

The passivated capillary section extending from the downstream side of the detector assembly was connected to a vacuum source (either house vacuum or a small, pulse-dampened diaphragm pump), and a differential pressure gauge was used to monitor the pressure in the system just upstream from the vacuum source. The flow rate, Q (ml/min), through the system varied linearly with pressure drop, ΔP (inches of water), according to the following equation: $Q = 0.070\ \Delta P$. All experiments were performed at a flow rate of 1 ml/min to maintain a low pressure drop and also to operate in a flow regime compatible with low-displacement pumps that might ultimately be used in a microanalytical system.

Several approaches to heating the PLOT traps were explored, including the use of silver paint, silver epoxy, and thin NiCr wire. None of these approaches was capable of providing rapid uniform heating along the length of the trap. In the end, precision bore CuNi tubing (Accumetrics, Royersford, PA) was used, which fit snugly around the PLOT capillary. CuNi tubes, 2-cm long, with the following radial dimensions were used: 0.635-mm o.d. × 0.432-mm i.d for the PLOT-Q trap and 0.935-mm o.d. × 0.671-mm i.d. for the PLOT-S trap. Wires were soldered to the ends of each tube for applying current. Each tube was first wrapped with one layer of Teflon tape and then a bare-wire, type-K thermocouple (0.002″ o.d., Omega Engineering, Stamford, CT) was placed against it and secured with several additional layers of Teflon tape.

For thermal desorption, the tube was heated via a programmable relay built in-house with AC current supplied from a Powerstat variable autotransformer (Superior Electric, Bristol, CT) adjusted to 6 V. Temperature was monitored with the readout module of a separate temperature controller (Model CN8500, Omega Engineering, Stamford, CT) whose control functions could not be applied to this system. The tube could be heated reproducibly to 200–205°C in ≤ 2 s. This temperature is 50°C less than the maximum temperature recommended by the manufacturers for operating the PLOT columns (assuming an inert gas matrix), and is also ~20°C higher than the boiling point of the least volatile vapor tested: DMMP. The preconcentrator tube cooled to about 70°C within a few seconds of switching off the heater power, and then gradually cooled to room temperature over the following 30 s.

2.4. Methods

Test atmospheres were prepared by injecting a known volume of liquid into a 5-l Tedlar bag (0.06-mm wall thickness) and diluting with dry N_2. For each vapor, four bags were prepared to span a modest concentration range, typically ~50–300 ppm. Blank responses were collected from bags filled with dry N_2 from a compressed gas cylinder. A small peak was consistently observed in the blank samples, which is attributable to water vapor that had permeated into the bags from the laboratory atmosphere (note: Tedlar is known to be highly permeable to water vapor). Upon thermal desorption, water co-eluted with MEK and TCE but eluted prior to toluene and *m*-xylene. Several blanks were collected over the course of an experiment and blank subtraction was performed as necessary prior to quantification. System temperature was not controlled but remained within the range of 19–22°C over the course of the study.

Initial tests with DMMP gave what appeared to be broad, poorly defined response peaks that eluted at the same time as water vapor. This was attributed, in part, to the poor sensitivity of the PIB-coated sensor to DMMP [34]. However, DMMP adsorption on the walls of the system, particularly the freshly exposed surface of the PLOT-Q capillary, was suspected to be contributory. In order to reduce wall adsorption throughout the system, a saturated atmosphere of the silanizing agent solution, DMDCS in toluene, was generated in a Tedlar bag and drawn through the apparatus for several minutes. This resulted in a very slight improvement in the sharpness of the observed response peaks and had no observable effect on the responses of the other solvent vapors. A similar treatment of the system was performed prior to testing the PLOT-S trap. Subsequent testing revealed that DMMP was not being desorbed from either type of trap at temperatures as high as 230°C. So, DMMP was not tested further.

Calibrations were performed by sampling for 1 min at 1 ml/min and then activating the preconcentrator heater relay manually. The subsequent sample was collected immediately after activating the heater for the first sample. Two to four replicates were performed at each concentration. There was no evidence of sample retention within the PLOT trap after desorption. Limits of detection were calculated as 3σ/sensitivity after blank subtraction, where σ is the short-term baseline noise.

Calibrations without preconcentration were performed by replacing the PLOT trap with a section of passivated capillary and measuring the net frequency shift (relative to the blank) after allowing sufficient time for establishment of sorption equilibrium. Measurements were repeated after exposure to N_2 and baseline recovery. Sensitivities were determined for all of the vapors over the same concentration ranges as used for the preconcentrated samples.

Breakthrough studies were performed with 1-cm sections of PLOT-Q and PLOT-S for each of the four test vapors at each of several concentrations. Additional testing with *m*-xylene was performed with a 1.5-cm PLOT-Q section at 120 ppm. In accordance with standard frontal analysis procedures [35], a sample of the test atmosphere was drawn through the system and the heater was activated to remove any trapped vapors. This marked the start of the breakthrough test for the subsequent sample. Sample collection was continued after breakthrough detection until a steady-state response was observed with the SAW sensor. For comparison with modeled results for the PLOT-Q, t_B (Eq. (2)) was defined as the time required for the sensor response to reach 10% of its maximum value (i.e., $C = 0.1C_0$) and was determined from the profile of sensor response versus time by graphical interpolation after accounting for any baseline drift. Additional tests were performed for *m*-xylene with the 1-cm PLOT-Q trap at one concentration by increasing the sampling duration in 1-min increments, desorbing collected samples, and assessing when the response curve became non-linear.

3. Results and discussion

3.1. Penetration modeling

Eq. (1) was used to construct Fig. 2, which plots the values of Q and L required to maintain $P \leq 0.01$ (i.e., 1% penetration) at two limiting values of D. The D values chosen, 0.040 and 0.15 cm^2/s, bracket the range of those for most volatile organic compounds in air at 25°C [36]. Note that P is independent of the capillary diameter, because for a given Q any increase in diameter will be offset by an increase in residence time. For a flow rate of 1 ml/min, a capillary as short as 3.2 mm can be used without suffering significant penetration for $D \geq 0.04$ cm^2/s. If L is fixed at, say, 1 cm, a flow rate as high as 6.3 ml/min can be tolerated without penetration of even the least diffusive vapors. For toluene, with $D = 0.085$ cm^2/s, a flow rate of about 13 ml/min could be used with a 1-cm capillary.

For integrated microanalytical systems, preconcentrators of rectangular dimensions are of potential interest because they can be constructed by micromachining or standard planar microfabrication methods [13]. Modeling

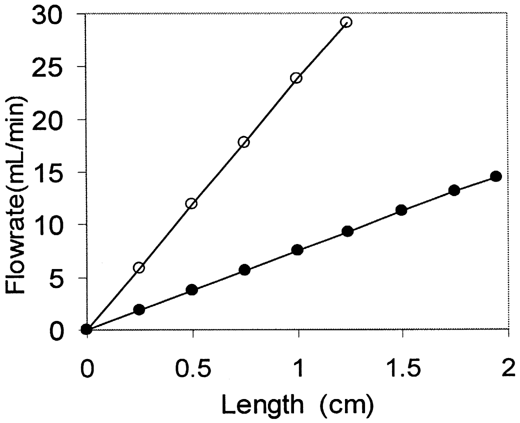

Fig. 2. Theoretical flow rate-length relationship required to maintain the penetration fraction below 1% for two limiting values of vapor diffusion coefficient: $D = 0.15$ cm^2/s (open symbols) and $D = 0.040$ cm^2/s (filled symbols).

indicates that for a 1-cm channel of rectangular cross-section having dimensions of 40×500 μm (c.s. area $= 2 \times 10^4$ μm^2), a flow rate of 50 ml/min could be tolerated while maintaining $P \leq 0.01$ for vapors with $D \geq 0.04$ cm^2/s, assuming all surfaces are adsorptive [23].

Comparing a preconcentrator with a circular cross-section 250 μm in diameter (c.s. area $= 5 \times 10^4$ μm^2) to that with a rectangular cross-section of similar area, the rectangular cross-section permits a higher sampling flow rate. This is because the collision frequency is determined by the narrowest dimension of the cross-section. Trap residence times become very short at such high flow rates, however, and may approach diffusion times required for vapor transport into the micropores of the adsorbent [37]. For reference, at a flow rate of 10 ml/min, a 1-cm trap of 250-μm diameter (circular cross-section) has a residence time of only 3 ms.

Selective preconcentration can be considered in the context of this modeling approach whereby the trap length or system flow rate could be adjusted to intentionally increase the fractional penetration of higher-molecular-weight vapors with smaller D values while retaining lighter more diffusive vapors. However, only marginal levels of preselection (20–30%) would be possible over the range of typical organic vapor D values. Preselection for vapors in the presence of aerosols, which have much lower diffusion coefficients, is feasible [23] and might provide a means of removing undesired ambient particulate matter from a microanalytical system with the PLOT traps. This would require bypassing system components downstream of the preconcentrator during sample collection [13].

3.2. Adsorbent breakthrough times

Experimental t_B values for the 1-cm PLOT-Q trap ranged from about 1 to 4 min and increased with decreasing vapor pressure among the different vapors. Similar values were observed with the PLOT-Q and PLOT-S traps for MEK and TCE while the t_B values for toluene and m-xylene with the PLOT-S trap consistently exceeded those with the PLOT-Q trap. The representative data presented in Table 2 are confined to relatively high exposure concentrations because of limitations in accurately assigning t_B values at the lower challenge concentrations. It was noted, however, that t_B decreased with increasing concentration for all of the vapors tested.

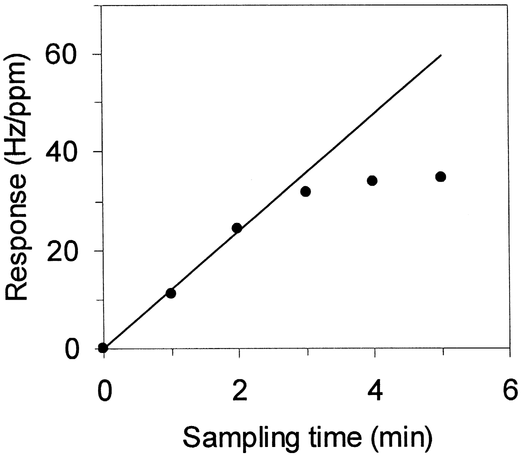

Fig. 3. Effect of sampling time (volume) on desorbed response maxima for m-xylene at 120 ppm. The apparent $t_B \cong 170$ s.

Eq. (2) predicts a linear increase in t_B with increasing adsorbent mass, W. Although the PLOT-S trap contains 29% more adsorbent, only toluene and m-xylene showed longer t_B values on the PLOT-S. While the increase in t_B for toluene follows expectations, that for m-xylene is much greater than expected. Surprisingly, the more polar PLOT-S does not appear to have relatively greater affinity for the MEK and TCE.

For both PLOT capillaries, the adsorbent polymer layer thickness is 8 μm and its bulk density is ~0.3 g/cm^3 according to the manufacturer. This yields an adsorbent mass (W in Eq. (2)) of 18.2 μg/cm of PLOT-Q (23.5 μg/cm of PLOT-S), and an effective adsorbent density (ρ_b in Eq. (2)) of 0.0496 g/cm^3 averaged over the entire capillary volume (i.e., accounting for the open bore of the PLOT-Q capillary). Using these data and the W_e and K_v values in Table 1, Eq. (2) was used to estimate t_B at the concentrations given in Table 2. No modeling was performed for the PLOT-S trap.

Table 2
Breakthrough time comparisons for 1-cm PLOT-Q and PLOT-S traps[a]

Vapor	Conc.[b] (ppm)	PLOT-Q t_B experimental (s)	PLOT-Q t_B modeled (s)	Model error (%)	PLOT-S t_B experimental (s)	Difference $(Q-S/Q)$ (%)
MEK	160	(70)[c]	65	−7	65	7
TCE	160	120	53	−56	112	7
Toluene	140	165	160	−3	204	−24
m-Xylene	120	240	182	−24	390	−63
m-Xylene[d]	120	170	182	−7	–	–

[a] 10% breakthrough values determined at a flow rate of 1 ml/min.

[b] Inlet vapor concentration.

[c] Value is uncertain due to baseline drift.

[d] Determined from thermally desorbed samples collected over increasing sample periods (see text and Fig. 3).

Table 3
Comparison of 10% breakthrough times for *m*-xylene with 1.5- and 1.0-cm PLOT-Q traps

Conc.[a] (ppm)	1.5-cm t_B (s)			t_B Ratio (1.5:1.0)	
	Exp.	Model	Error (%)	Exp.	Model
120	355	295	−17	1.5	1.6
160	350	302	−14	1.7	1.6

[a] Inlet vapor concentration

The modeled values of t_B underestimate the measured values in all cases for the PLOT-Q trap. Errors for the more volatile MEK and TCE can be attributed, in part, to the fact that the trap is at elevated temperature during the initial part of the collection period. If a portion of the incoming sample is lost due to poor adsorption efficiency at the elevated temperatures, this might go undetected and would lead to an increase in the apparent value of t_B. Some evidence to support this was observed with MEK where a baseline drift was observed about 15 s after the start of sampling. The less volatile vapors toluene and *m*-xylene would not be affected as much by this factor. Agreement between modeled and measured values for toluene is quite good, while the measured values for *m*-xylene are, again, much higher than expected. As shown below, the *m*-xylene response peaks show significant tailing, suggesting that adsorption on system surfaces upstream from the sensor (e.g., the glass–wool plug inserted between the preconcentrator and the sensor cell) may be important. Initial breakthrough may go undetected due to retention on these surfaces.

As a check on t_B for *m*-xylene, a series of additional experiments was performed involving increasing the sampling time from 1 to 5 min in 1-min increments and thermally desorbing the samples. The results, shown in Fig. 3, indicate that a sampling time of up to ~ 2.5 min leads to proportional increases in sensitivity. At sampling times ≥ 3 min, breakthrough of the *m*-xylene is apparent. The 10% t_B estimated from these data is ~ 170 s, in reasonable agreement with the modeled value of 182 s for this concentration (see Table 2). The discrepancy between this experimental t_B value and that determined by frontal analysis supports the notion that wall adsorption and/or detection limit problems lead to overestimates of t_B by frontal analysis. Thus, the Wheeler model appears to provide useful breakthrough time estimates.

For MEK and TCE, t_B values at concentrations > 220 ppm declined sharply, indicating that the adsorbent is approaching saturation (data not shown). Thus, vapors more volatile than MEK are not likely to be trapped quantitatively in a 1 ml sample, even at lower concentrations. The relatively long t_B values for toluene and *m*-xylene suggest that for less volatile vapors larger sample volumes could be collected, leading to commensurate increases in sensitivities (see below). However, the results for DMMP (see Experimental) show that sorption of higher boiling vapors may not be completely reversible at attainable desorption temperatures.

For *m*-xylene, additional modeling and frontal analyses with the PLOT-Q trap were performed to compare the performance of 1.5-cm and 1.0-cm trap lengths (Table 3). Errors in modeled t_B values for the 1.5-cm trap are similar to those found for the 1-cm PLOT-Q by frontal analysis. However, t_B values increase with length to the extent predicted by the model.

3.3. Response profiles, sensitivities, and LODs

Fig. 4 shows response profiles for *m*-xylene and TCE on the PLOT-Q and PLOT-S 1-cm traps at similar concentrations. The profiles for each vapor are similar on both traps. TCE elutes as a sharp, narrow peak at all concentrations with only slight tailing. Similar results were observed for MEK and toluene. *m*-Xylene, on the other hand, shows significant tailing and a much stronger dependence of peak width on concentration, with lower concentrations yielding significantly broader peaks. The peak width at half maximum provides a combined measure of desorption efficiency and sample transport through the system. The ranges in Table 4 for each vapor confirm that MEK, TCE, and

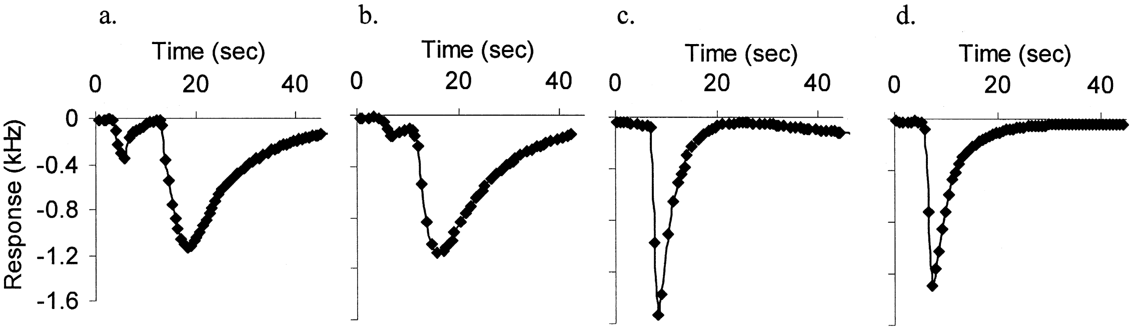

Fig. 4. Response profiles for 1-ml samples of (a) 115 ppm of *m*-xylene from PLOT-S; (b) 120 ppm of *m*-xylene from PLOT-Q; (c) 150 ppm of TCE from PLOT-S; (d) 130 ppm of TCE from PLOT-Q. The response maximum in (d) appears larger than expected (see Table 5) because of a large blank (water vapor) response.

Table 4
Response characteristics of vapor samples thermally desorbed from 1-cm PLOT traps

Vapor	Conc. range (ppm)	Peak width at half-maximum (s)		Elution time (s)	
		PLOT-Q	PLOT-S	PLOT-Q	PLOT-S
Toluene	50–250	6–7	4–6	4–5	5–6
m-Xylene	40–250	10–17	12–21	10–12	16–20
TCE	60–330	2–5	3–5	2–4	2–4
MEK	60–330	2–5	3–4	2–3	2–3

toluene are all more efficiently desorbed and transported than *m*-xylene.

Elution times range from 1 to 20 s after actuation of the preconcentrator heater, increasing with decreasing solvent vapor pressure. Complete separation of toluene and *m*-xylene from each other and from the other two vapors would be expected from mixture analyses. MEK and TCE co-elute with each other and, as stated above, with water vapor.

Response maxima measured from the leading edge of each peak were reproducible to within 10% among duplicate or triplicate samples and were used to construct calibration curves from which sensitivity values were derived by linear regression with forced zero (Table 5). Responses were linear over the concentration ranges examined. Coefficients of determination (r^2) were all ≥ 0.98. Sensitivities increase (LODs decrease) with decreasing solvent vapor pressure as expected [38,39]. Greater sensitivity with the PLOT-S trap is observed for both MEK and TCE, with the effect being quite significant for TCE. This belies the similarity of the TCE peak shapes and elution times for both traps presented in Table 4. While the explanation for the large difference in TCE sensitivities between the two traps is unclear the practical significance is that use of two different traps may provide a means of differentiating vapors based on their relative responses.

Sensitivities without preconcentration were also constant over the concentration ranges examined. The sensitivity enhancements from preconcentration range from about 3- to 9-fold for a 1-ml sample volume and increase in proportion to the sample volume as shown for xylene (see Table 5 and Fig. 3). LODs are reduced in proportion to the sensitivity enhancements and range from 1 to 8 ppm for these solvents. These increases in sensitivity are quite modest. However, the sensitivities *per unit volume of sampled air* are greater than those reported for other systems employing adsorbent preconcentrators with SAW sensor arrays [4,5,12]. This is attributable to the low dead volume of the current system as well as the relatively narrow peak widths obtained here (with the exception of *m*-xylene), and serves to emphasize that with polymer-coated sensor systems whose responses are based on partitioning, reductions in sample size can improve sensitivity [6,13]. This scaling advantage is not without limit, however, since eventually the sample volume will be reduced to the point where there is insufficient mass in the sample to reach true sorption equilibrium within the polymeric sensor coating. Further improvements in sensitivity with this system can be obtained by increasing the sample volume up to the point of adsorbent breakthrough — Table 5 shows for *m*-xylene that doubling the sample volume doubles the sensitivity and halves the LOD.

4. Conclusions

This preliminary study has established the feasibility of PLOT capillaries as thermally desorbable vapor preconcentrators in microanalytical systems. Common solvent vapors can be efficiently trapped, desorbed, and detected from a 1-ml air sample at low-ppm concentrations in ≤ 60 s at a

Table 5
Vapor sensitivities and limits of detection with and without 1-cm PLOT traps[a]

Vapor	Sensitivity[b] (LOD)[c]				Sensitivity enhancement factor	
	No PCT	PLOT-Q	PLOT-S	Q:S ratio	PLOT-Q	PLOT-S
MEK	0.5 (26)	1.6 (8.1)	1.9 (6.8)	0.84	3.2	3.8
TCE	0.8 (16)	4.7 (2.7)	7.3 (1.8)	0.64	5.9	9.1
Toluene	1.2 (11)	6.9 (1.9)	6.6 (2.0)	1.05	5.8	5.5
m-Xylene	2.4 (5.4)	13 (1.0)	12 (1.1)	1.08	5.4	5.0
Xylene[d]	2.4 (5.4)	26 (0.5)	–	–	10.8	–

[a] Values for PLOT traps are based on a 1-ml samples.
[b] Hz/ppm.
[c] ppm.
[d] 2-ml sample.

flow rate of 1 ml/min using an in-line polymer-coated SAW sensor.

Increases in flow rate would lead to commensurate decreases in cycle time and modeling indicates that traps with rectangular cross-sections permit higher flow rates to be used than those with circular cross-sections. At very high flow rates, however, residence times may approach diffusion times into the micropores of the wall-coated polymer adsorbent, which would reduce the effective adsorption capacity. Pressure drops within the system may also become excessive at high flow rates. Limitations on the displacement volumes of micromachined pumps that might ultimately be used in microanalytical systems employing such PLOT traps may limit the flow rates and suction pressures achievable in practice.

The capacity of the adsorbent dictates the total sample volumes that can be collected, the maximum concentrations that can be analyzed, vapor sensitivities, and LODs. For the vapors tested here, allowable sample volumes for a 1-cm PLOT trap ranged from 1 to 6 ml, depending on the vapor, and increased in proportion to the trap length (adsorbent mass). The modified Wheeler equation provided reasonably accurate estimates of breakthrough times, once experimental cofactors were taken into account.

Sharp, relatively symmetric response profiles were obtained for three of the five vapors. Broad, tailing peaks observed for *m*-xylene are attributable to slow desorption and/or adsorption on system surfaces downstream from the PLOT trap. Peak widths showed a significant dependence on concentration for *m*-xylene as well. Neither of these effects was observed with vapors more volatile than *m*-xylene. The relatively non-volatile vapor, DMMP, was efficiently trapped with both the PLOT-Q or PLOT-S traps but could not be desorbed at temperatures as high as 230°C. Increasing the desorption temperature and the heating rate of the trap should improve the desorption efficiencies and sensitivities for all vapors. In this study, desorption temperatures were maintained below the maximum operating temperature of the PLOT capillaries recommended by the manufacturer (250°C), since further increases would risk decomposition of the porous polymer adsorbents, particular when operated in an air matrix. Note also that data acquisition rates may become a limiting factor as peak widths become narrower [6].

The variation of elution times with vapor volatility may be advantageous, as noted by others [4–6,12,14,16]. But, low-boiling vapors co-elute with water vapor, demanding a sensor or sensor array that is capable of discriminating among such vapor mixtures. Observed differences in TCE peak profiles and sensitivities between the PLOT-Q and PLOT-S traps warrant further investigation, as this suggests a means of improving selectivity via the preconcentrator: a microanalytical system with dual parallel sampling trains [13] would provide different responses for the same TCE concentration. Additional work is also needed to experimentally characterize the effects of increased sampling flow rates on system performance and to address the preconcentration and analysis of vapor mixtures.

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