Low-flow active and passive sampling of VOCs using thermal desorption tubes: theory and application at an offset printing facility

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While air sampling techniques using adsorbent-based collection, thermal desorption and chromatographic analysis have found a niche in ambient air sampling, occupational applications have been more limited. This paper evaluates the use of thermal desorption techniques for low flow active and passive sampling configurations which allow conveniently long duration sampling in occupational settings and other high concentration environments. The use of an orifice enables flows as low as 0.5 ml min\(^{-1}\) and sampling periods up to several days without significant biases. A model is used to predict sampling rates of a passive sampler encompassing an orifice, a void space, glass wool, and the adsorbent. Laboratory and field tests conducted at a commercial offset printing facility, which contained a variety of volatile organic compounds (primarily aromatic but also a few chlorinated and terpene compounds at levels from 1 to 67,000 ppm), are used to evaluate the approach. Tenax GR and Carbosieve SIII, both singly and together, were employed as adsorbents. Side-by-side tests comparing high flow, low flow and passive samplers show excellent agreement and high linearity (\(r = 0.95\)) for concentrations spanning nearly five orders of magnitude. Active samplers were tested at flows as low as 0.5 ml min\(^{-1}\), compared to typical flows up to 40 ml min\(^{-1}\). Passive samplers demonstrated a linear range and agreement with predictions for adsorbate loadings from \(~1\) ng to nearly 10 \(\mu\)g. Using a chemical mass balance receptor model, concentrations in the facility were apportioned to solvents, inks and other indoor and outdoor sources. Overall, the use of low flow active and passive sampling approaches employing thermal desorption techniques provides good performance and tremendous flexibility that facilitates use in many applications, including workplace settings.

Aim of investigation

Both passive and active sampling techniques have long been used to collect airborne volatile organic compounds (VOCs) present in the workplace at ppm levels. Passive sampling has gained popularity since no pump is needed to collect samples; procedures such as flow calibrations are eliminated (lowering expenses); large numbers of passive samplers are easily deployed; wearer acceptance is less of an issue than pumped samplers; and integrated samples can be collected over a range of sampling periods. In addition, operation is very simple, mathematical models for diffusion samplers are well established,\(^1\)–\(^3\) appropriate designs are resistant to environmental factors such as temperature, precipitation, sunlight, wind, humidity,\(^4\)–\(^6\) methods are available for an increasing set of target compounds (e.g., VOCs, aldehydes, ozone, and nitrogen dioxide), and sampling rates and other parameters have been validated for many compounds.\(^6\) Most applications of passive or diffusive samplers have utilized adsorbents in a badge configuration achieving sampling rates of 25 to 35 ml min\(^{-1}\). Although this sampling rate rarely limits workplace sampling, it may restrict use to longer sampling times and/or higher concentrations. For example, NIOSH Method 4000 is applicable for toluene concentrations from 20 to 200 ppm with a minimum sample time of 15 min (for 200 ppm) and maximum sample time of 8 h.\(^7\)

Active adsorbent sampling is also well established in occupational and environmental applications. Active sampling permits control over the sampling rate and sample averaging time, and thus is useful to measure peak, ceiling, and 8 h averages. As examples, NIOSH method 1500 for hydrocarbons with boiling points between n-pentane and n-octane specifies sampling flow rates from 10 to 200 ml min\(^{-1}\) and sample volumes from 2 to 30 l; method 1501 for aromatic hydrocarbons uses flow rates of 10 to 1000 ml min\(^{-1}\) and sample volumes of 1 (most cases) to 100 l (naphthalene); and method 1003 for halogenated hydrocarbons specifies rates from 10 to 200 ml min\(^{-1}\) and volumes from 0.1 to 150 l.\(^7\) These active adsorbent sampling methods, as well as most passive sampling approaches, use charcoal as an adsorbent, carbon disulfide (CS\(_2\)) for chemical desorption, and gas chromatography (GC) and flame ionization detection to quantitate VOCs.

Thermal desorption has made great strides in method detection limits, precision and automation. Thermal desorption recovers essentially all of the trapped adsorbate thus greatly increasing sensitivity, and the method has gained wide acceptance in a variety of applications.\(^5\)--\(^8\) In addition to achieving high performance,\(^9\) the method is flexible and convenient, large ranges of target compounds and analytical detectors are practical since solvent use is eliminated, and high laboratory throughput can be achieved using automated equipment. Even though an international standard, which addresses sampling in workplace air, has been developed recently for thermal desorption and GC analysis with active sampling\(^10\) and a similar standard for passive sampling is almost ready, these methods have been less commonly employed in occupational applications because airborne concentrations are often high, allowing only short sampling periods.

This paper describes low-flow active and passive samplers employing single and dual adsorbent thermal desorption tubes which allow conveniently long sampling periods in workplace conditions. The performance of these samplers is evaluated using theoretical predictions and results of laboratory and field
Most adsorbents suitable for thermal desorption have lower retention volumes and specific surface areas than charcoal, thus to maintain a constant sampling rate, adsorbents should be selected to keep the adsorbat concentration at the adsorbent surface as low as possible during the sampling period. Tenax TA and GR are the most commonly used adsorbents; other contenders include Chromosorb 106, graphitized carbon black (Carbopack and Carbotrap), and carbon molecular sieves (Carboxen and Carbosieve). Vahdat et al. estimated sorption capacity, thermal desorption efficiency, and breakthrough times for four adsorbents, while Cao and Hewitt evaluated four adsorbents for passive sampling. Using Perkin Elmer diffusion tubes, no obvious differences among adsorbents were found for C6-C8 hydrocarbons, but better performance for Chromosorb 106 for the C3 compound tested (isoprene). These tests were conducted at concentrations between 0.1 and 0.2 ppm and durations up to 6 h, yielding exposure doses between 10 and 50 ppm-min. Much higher doses may occur in workplace applications, for example, a sampling range to ~48,000 ppm-min is needed for a VOC with an 8 h TLV of 100 ppm.

Active sampling using thermal desorption

Recently, thermal desorption and cryofocusing techniques have become fairly standardized for ambient and indoor air sampling, and reference methods and standards suitable for low (ppb) concentrations have been developed. US EPA recommends distributed volume samples, specifically sample flow rates of 16.67 and 66.7 ml min \(^{-1}\), for 2 h samples of volumes 1 and 4 l, respectively. The ISO standard recommends air volumes between 1 and 10 l, selected to be within the safe sample volume (<70% of the 5% breakthrough volume) and to achieve a total uptake <1 mg; specific flow rates are not recommended, although it comments that breakthrough volumes are substantially reduced at flow rates <5 and >500 ml min \(^{-1}\). With Tenax GC, Brown and Purnell used an indirect method to estimate safe sampling volumes, and on the basis of theoretical plate numbers, suggested that flow rates should be held between 5 and 600 ml min \(^{-1}\) (for a 4.5 mm id tube). In both indoor air quality (office buildings) and ambient applications, total VOC concentrations are generally <100 μg m \(^{-3}\), representing at most an adsorbate mass of ~400 ng in a 4 l sample. In comparison, concentrations in occupational settings may be much greater, for example, a TLV of 100 ppm (~200 mg m \(^{-3}\)) represents a 2,000-fold increase over (high) ambient or indoor levels. Considering the reduced capacity of thermally-desorbable adsorbents and the efficient extraction and delivery of the adsorbate to the analytical system, it is clear that sample volume must be greatly reduced to limit breakthrough, maintain a constant sampling rate, and stay within the calibration range of the GC’s detector.

Advantages of thermal desorption

Thermal desorption has advantages for both active and passive sampling: a very large dynamic range; applicability to a broad set of compounds and adsorbents; elimination of solvent use and technician complaints associated with CS2 and other toxic materials; reusability of the sampling device; reasonable cost; availability of automated desorption and analysis systems that achieve high throughput and precision. Dynamic range and sensitivity are particularly significant issues. Currently, active sampling thermal desorption methods require <1 ng of analyte to achieve detection limits of ~0.1 ppb. If the dynamic range can be increased to permit measurements of 100 to 1000 ppm, then both workplace, ambient and possibly process measurements can be made using the same technique and hardware. This will enhance the comparability, cost-effectiveness and quality of these monitoring programs.
Description of the experimental procedures

Sampler and adsorbents

VOC sampling employed stainless steel tubes of dimensions 10 cm length, 6 mm od, 4 mm id, with tapered screw threads on both ends (Scientific Instrument Services, Inc., Ringoes, NJ) (Fig. 1). These are the standard tubes used by the automated desorber described later under ‘Sample Analysis’. Adsorbent selection was based on recommendations for ambient air sampling. Tubes were packed at the upstream (sampling) end with 3 mm silanized glass wool, 160 mg 60/80 mesh Tenax GR (polyester-phenyl) ether with 23% graphitized carbon, followed by 3 mm silanized glass wool, 70 mg Carbosieve SIII (Supelco, Inc. Bellefonte, PA, 60/80 mesh), and finally 3 mm silanized glass wool at the downstream end (Fig. 1). The adsorbent bed was positioned 2.0 cm from the tube end. For comparison purposes, another set of tubes was packed with only Tenax GR. Packed tubes were conditioned at 325°C in a 24-tube conditioning oven (Model A-24, Scientific Services, Inc., Ringoes, NJ) for 6 h with a 25–50 ml min⁻¹ reverse flow of high purity (99.999%) helium. After conditioning, tubes were sealed with stainless steel caps with Teflon® seals screwed onto both ends, wrapped in previously baked aluminum foil, and stored in a glass jar at 4°C.

Passive sampling

During passive and low flow active sampling, the tube’s upstream cap was replaced by a 0.102 cm diameter (0.25 cm long) orifice with a Teflon® seal (Fig. 1). Originally designed for use in tube conditioning, the orifice reduced the diffusive flux and helped to minimize any air currents in the diffusive path within the sampler. Based on the following modeling, the orifice decreased the sampling rate by 2-fold.

Theoretical passive sampling rates

The determination of sampling rates and sorbent issues has been reviewed elsewhere. The following extends this to multilayer sections. The flux $F$ ($\mu$g s⁻¹) of an adsorbate (VOC) to an adsorbent is derived using Fick’s First Law

$$F = -D \frac{dC}{dz} \approx -DA \frac{\Delta C}{L}$$

where $A =$ cross-sectional area of the sampler (cm²), $D =$ effective diffusion coefficient (cm² s⁻¹), and $\frac{dC}{dz} =$ concentration gradient ($\mu$g cm⁻²). With a uniform gradient, $\frac{dC}{dz} = \frac{\Delta C}{L}$, where $\Delta C$ is the concentration difference between air just outside the sampler and the concentration near the surface of the adsorbent, and $L$ is the diffusion path length. The term $D A L$ (cm² s⁻¹ or ml min⁻¹) has been termed the diffusive conductance or simply the sampling rate.

The effective diffusion coefficient $D$ may differ from the ‘free-air’ diffusion coefficient $D_0$ due to obstacles in the diffusion path such as a diffusion cap, windscreen, or glass wool such that:

$$D = \theta \tau D_0$$

where $\theta$ is the effective gas phase area for diffusion, $\tau$ is the air phase tortuosity accounting for the “tortuous” diffusion path in porous media, and $D_0$ is the free-air diffusion coefficient of the specific vapor (cm² s⁻¹). Conceptually, $\theta$ is the ratio of the straight path length to the tortuous path length, thus, $\tau \leq 1$. Both $\theta$ and $\tau$ are media properties. Free-air diffusion coefficients $D_0$ available for many vapors in air at 25°C are adjusted to temperature $T$ (K).

$$D_T = D_0(T/298)^{0.5}$$

The diffusive sampler used in this study included the 0.075 cm diameter orifice, a 1.7 cm section of the larger (0.4 cm diameter) tube, then a 0.3 cm length wad of compressed glass wool in the tube to hold the adsorbent in place. Thus, VOC diffusion into the tube may be conceptualized through first the open (completely air-filled) orifice, into the open section of the tube, then into the tube section filled with glass wool, and then finally onto the adsorbent. The harmonic average of the sampling rate for the discrete sections gives the total uptake rate:

$$F = - \left( \frac{A_1 D_0}{L_1} + \frac{A_2 D_0}{L_2} \right)^{-1} \Delta C$$

where $A_1$, $L_1$, $A_2$, and $L_2$ are the cross-sectional area and length, respectively, of the orifice, $A_3$ and $L_3$ are dimensions of the open section of the tube, $A_4$ and $L_4$ are dimensions for the tube section incorporating additional resistance due to the glass wool with effective gas area $\theta$ and tortuosity $\tau$. Finally, because the airborne concentration at the adsorbent is assumed to be negligible and the space measured is assumed to be well-mixed, thus minimizing any depletion of VOCs in the proximity of the sampler, $\Delta C \approx C$, where $C =$ concentration in the space. The uptake rate for any particular VOC is then given by eqn. (4) with tube-specific parameters $A_1$, $L_1$, $A_2$, $L_2$, $A_3$, $L_3$, $\theta$, and $\tau$, and VOC- and temperature-specific parameter $D_0$, which is based on a literature value of $D$ adjusted to the temperature of interest by eqn. (3). For the experiments reported later, $A_1 = 0.00817$ cm², $L_1 = 0.25$ cm, $A_2 = 0.126$ cm², $L_2 = 1.7$ cm, $A_3 = 0.126$ cm², $L_3 = 0.3$ cm; $\theta = 0.8$, and $\tau = 1.5$. $N$ and $\tau$ are estimated values, based on flows through porous media such as soils. At 20°C, $D_0$ ranges from 0.302 cm² s⁻¹ for a 3 carbon compound (n-propane) to 0.067 for a 10 carbon compound (n-decane). In eqn. (4), this yields sampling rates from 0.083 (n-decane) to 0.340 (n-propane) ml min⁻¹.

In addition to reducing diffusion fluxes, the orifice reduces any mixing or air currents due to high velocities in the sampler’s vicinity that might effectively shorten the diffusion path length and thus increase diffusional fluxes. This effect is difficult to predict theoretically since airflow and turbulence in the region of the tube inlet is unknown. Thus, the orifice

Fig. 1 Schematic of dual bed sorbent tube with orifice and end cap installed. Not to scale.
Table 1: Calculated sampling rates for sorbent tube with orifice (3 section tube including orifice, open section and glass wool retainer) and standard tube (2 section tube including same open section and same glass wool retainer). Porosity, tortuosity, diffusion coefficient and areas not applicable for totals

<table>
<thead>
<tr>
<th>Tube with orifice</th>
<th>Orifice</th>
<th>Open tube</th>
<th>Retainer</th>
<th>Total</th>
<th>Standard tube</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>1.000</td>
<td>1.000</td>
<td>0.800</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tortuosity</td>
<td>1.000</td>
<td>1.000</td>
<td>1.500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effective diffusion coefficient/cm² s⁻¹</td>
<td>0.075</td>
<td>0.075</td>
<td>0.040</td>
<td></td>
<td>0.250</td>
<td>0.093</td>
</tr>
<tr>
<td>Section radius/cm</td>
<td>0.051</td>
<td>0.200</td>
<td>0.200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Section length/cm</td>
<td>0.250</td>
<td>1.700</td>
<td>0.300</td>
<td>2.250</td>
<td>2.000</td>
<td>2.000</td>
</tr>
<tr>
<td>Section area/cm²</td>
<td>0.008</td>
<td>0.126</td>
<td>0.126</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sampling rate/ml min⁻¹</td>
<td>0.148</td>
<td>0.335</td>
<td>1.012</td>
<td>0.093</td>
<td>0.252</td>
<td></td>
</tr>
</tbody>
</table>

The uptake rate estimated by eqn. (4) is the theoretical steady-state rate achieved after sufficient time has passed. The time needed to approach steady-state conditions, \( t_{ss} \), can be estimated as:

\[
t_{ss} = L^2/(6D)
\]

where \( L \) is the diffusion path length. Given the short dimensions of the sampler (\( L \approx 2 \text{ cm} \), \( t_{ss} \) is small (\(< 20 \text{ s})

Many variants of eqn. (5) exist in the hygiene literature, e.g.,

\[
t = \frac{L^2}{iD} \quad \text{and} \quad t = 1.5 \frac{L^2}{iD}
\]

for passive samplers to reach steady-state conditions, while \( t = \frac{L^2}{iD} \) has been called the ‘response time’, defined as the average residence time of a molecule in the sampler’s diffusion zone. Despite potentially longer times given by these (and other) formulations, these lag periods have been shown not to affect sampling results.

Low flow active sampling

As mentioned, thermal desorption requires the collection of only ng quantities of compounds on the adsorbent, and small sample volumes are needed to limit breakthrough and stay within the calibration range of the GC’s detector. However, the risk of diffusion of vapors onto the adsorbent increases as the active sample flow rate is reduced. For this reason (as well as the low number of theoretical plates that decreases breakthrough volumes) Brown and Purnell have suggested that very low flow rates (\(< 5 \text{ ml min}^{-1} \)) should not be used. A simple way to limit diffusional uptake uses an orifice, as described above for the passive sampler. The 0.075 cm diameter orifice reduces the maximum diffusional sampling rate by approximately half (to 0.096 ml min⁻¹, Table 1), thus reducing possible errors due to diffusion. In the passive sampler, the orifice also acts as a windscreen. At these flow rates and assuming a 2 l sample, a volume that has been shown to provide good performance even under humid conditions, sampling periods up to several days are practical.

Laboratory study

A sequence of laboratory tests was used to evaluate the passive sampler. Challenge concentrations were prepared in a 10 l glass vessel covered by a metal lid with fittings for insertion of sorbent tubes, syringes, etc. An open petri dish containing 30 ml of a solvent ‘wash’, a commercial mixture composed primarily of 10 aromatic hydrocarbons (the predominant mixture found in the field study, described below) was placed inside the vessel. Equilibrium between the liquid and vapor phases was facilitated by a small electric fan suspended in the middle of the vessel. This headspace system was allowed to equilibrate at ~25 °C for ~2 h prior to sample collection. Concentrations in the vessel were determined by collecting a 100 µl headspace sample using a gas-tight syringe before and after the passive sampling tests. The headspace sample was then transferred to a packed sorbent tube using a stainless steel ‘tee’ type loader (Scientific Instrument Services, Ringoes, NJ) and a helium flow rate of ~40 ml min⁻¹ through the tee. Loaded tubes were analyzed by the thermal desorption GC-MS method described later. Concentrations of most compounds were maintained within 20% by this simple system. Somewhat larger changes were noted for some compounds at the highest concentrations, e.g., 1,2,4-trimethylbenzene, probably due to temperature changes over the test period.

Passive samples of the solvent mixture headspace were collected installing the orifice on the tube end containing the Tenax GR, capping the other end, and inserting the tube and orifice ~6 cm into the sampling vessel. Sample durations of 1, 3, 5 and 10 min were used to achieve a range of loadings. Most tests used the dual bed (Tenax GR + Carbosieve II) sorbent tube. For comparison, 5 min samples were also collected on tubes containing only Tenax GR.

Field study

Measurements were made at a commercial offset lithographic printing facility located in Michigan. This 1,115 m² facility has 8 presses and areas for the presses, sorting of printed material, typesetting (computer), reception and offices. On a typical day, 30 employees staff the facility. Air quality measurements were collected using passive and active (pumped) adsorbent tube sampling. Passive and active samples were collected from 8-10 am and 12:30-2:30 pm on six Fridays in December.
through February 2001 in the pressroom between the row of presses and the air return for the space. In addition to the specified VOC measurements, total VOC (TVOC) levels throughout the facility were surveyed 4 to 5 times daily using a continuous photo-ionization detector (PE Photovac, Markham, Ontario) calibrated to 100 ppm of isobutylene. Outdoor VOC samples were collected in 22 ml septum-equipped vials containing 5 ml of solvent at 25 °C. The vapor sample was then injected into a sorbent tube using the stainless steel “tee” loader described earlier. The VOC composition of three types of inks and a varnish used at the facility were analyzed similarly, except that headspace samples were taken at a slightly elevated temperature (37 °C).

Sample analysis

Tubes were analyzed within several days of collection using an automated short-path thermal desorption/cryofocusing system (Model 2000, Scientific Instrument Services, Ringoes, NJ) mounted above the injector/septum area of the gas chromatograph-mass spectrometer (GC-MS, Model 6890/5973 running Chemstation, G1701BA, Version B.01, Hewlett-Packard, Palo Alto, CA). A complete description of the method and its performance is given in Peng and Batterman.9 In brief, the system provides automated thermal desorption of up to 12 adsorbent tubes. After a 1 min dry purge (40 ml min⁻¹ of GC carrier gas) to remove excess water, tubes are heated to 200 °C and the sample is desorbed for 5 min at 10 ml min⁻¹ and transferred to the GC inlet via a ‘short-path’ 3.5 cm long stainless steel side-port needle previously screwed onto the sorbent tube. Using a split ratio of 10:1, the sample is collected on a cryofocusing trap at the head of the column, previously cooled to −140 °C. After 5 min desorption, the sample is removed from the GC flow path and the cryotrap is rapidly heated to 250 °C, providing a narrow injection band that enhances separation and resolution of compounds. Excellent separation of all target compounds was achieved using a 30 m × 0.25 mm id column with 0.25 μm film thickness of 5% diphenyl–95% dimethylsiloxane copolymer (HP-5MS, Santa Clarita, CA), and an oven temperature program starting at 8–10 am and 12:30–2:30 pm on each sampling day using active presses and the air return for the space. In addition to the 16 solvent ‘wash’ samples, injected into sorbent tubes as 2 μl dilutions containing from 3 to 130,000 ng of the solvent dissolved in pentane. Eqn. (6) increases the adjusted peak area as C_adj approaches or exceeds k. For most determinations, eqn. (6) did not alter results since C_adj ≈ k. Fig. 2 shows the MS response as a function of area counts relative to the response well within the linear range (<40 ng injection of individual VOCs). Points on the fig. show the various VOCs in the solvent; the line shows the attenuation given as the inverse of eqn. (6). For the largest injections, attenuation can exceed 90%. Fig. 2 shows that eqn. (6) fitted all tested compounds and provided an excellent fit for even large loadings, e.g., 180 μg injection of the solvent wash where C_adj = 6 × 10³ for 1,2,4-trimethylbenzene. The adjustment effectively linearized the MS response for all target compounds and yielded a useful dynamic range that exceeded four orders of magnitude.

Results – laboratory study

Precision

In the chamber tests of the passive sampler, duplicate or triplicate replicates obtained a mean precision of 17% and 12% for 5 and 10 min samples, respectively (Table 2). Of the 11 compounds measured, n-hexane had inconsistent reproducibility as its peaks often co-eluted with a branched hexane isomer (2-methyl pentane). Eliminating hexane, the chamber tests showed high precisions, averaging 14%. Sources of

\[
C_{adj} = C_{init}(k + C_{init})/k \tag{6}
\]

where C_adj = the adjusted peak area, C_init = the initial (reported) peak area from the MS, and k = 3.8 × 10⁷. Parameter k was selected to match responses for high concentration compounds found in analyses of 16 solvent ‘wash’ samples, injected into sorbent tubes as 2 μl dilutions containing from 3 to 130,000 ng of the solvent dissolved in pentane. Eqn. (6) increases the adjusted peak area as C_adj approaches or exceeds k. For most determinations, eqn. (6) did not alter results since C_adj ≈ k. Fig. 2 shows the MS response as a function of area counts relative to the response well within the linear range (<40 ng injection of individual VOCs). Points on the fig. show the various VOCs in the solvent; the line shows the attenuation given as the inverse of eqn. (6). For the largest injections, attenuation can exceed 90%. Fig. 2 shows that eqn. (6) fitted all tested compounds and provided an excellent fit for even large loadings, e.g., 180 μg injection of the solvent wash where C_adj = 6 × 10³ for 1,2,4-trimethylbenzene. The adjustment effectively linearized the MS response for all target compounds and yielded a useful dynamic range that exceeded four orders of magnitude.

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variation include the relatively short sampling period, which increased errors associated with tube insertion and timing; temperature changes (1–2 °C) in the laboratory during the tests, which affected headspace concentrations; analytical uncertainties (discussed earlier); the relatively small sample size; and variation in packing the sorbent tubes. With respect to the last factor, potentially 1 or at most 2 mm variation in the diffusion path length may have resulted from variation in the thickness of the glass wool used to retain the sorbent. In active sampling, this variation is insignificant, however, in passive sampling, a 1 mm variation in the glass wool thickness would change the sampler’s total uptake rate by 3%. This error can be reduced by more accurately positioning the sorbent bed, and a tolerance of 0.03 cm is suggested, which would limit errors from this factor to about 1%.

Single versus dual-bed sorbent tubes

Comparisons between uptakes for tubes packed with and without Carbosieve III showed no significant differences based on a paired t-test (p = 0.90). This indicates that this adsorbent is not taking-up VOCs, as expected, since breakthrough of the first adsorbent (Tenax GR) is unlikely, and the longer and tortuous diffusive path through the fine grained Tenax would reduce the sampling rate onto the Carbosieve. Further, Carbosieve is mainly used to capture C4 and lighter hydrocarbons, which the solvent wash did not contain in significant amounts. If light VOCs were present, uptake on the Carbosieve might occur and the development and calibration of a dual bed adsorbent model would be required. In the present experiments, however, the passive sampler’s performance was unaffected by the presence of a second adsorbent (using a tube designed for a different application). Subsequent analyses combine results from both tube styles.

Accuracy

Exposures in the chamber tests varied over four orders of magnitude since the sampling time varied from 1 to 10 min, and the VOC headspace composition varied from 4 mg m⁻³ (ethyl benzene) to 5,212 mg m⁻³ (1,2,4-trimethylbenzene). Fig. 3 shows a strong linear (r = 0.97) relationship between the measured and predicted uptake on the passive sampler for all adsorbent loadings, which ranged from ~1 to 3,700 ng. Predicted concentrations were based on the sampler dimensions, VOC-specific diffusion coefficients, and average concentrations in the headspace as measured using active samplers. All but two observations were within a factor of 2 of predictions based on the diffusion model, specifically, a hexane determination (due to chromatographic interferences mentioned above) and a low toluene value, ~1 ng.

The laboratory tests used very high concentrations, levels that would not be found in environmental or occupational environments, with the exception of confined spaces such as tanks. Given the high concentrations, sampling times were very short to keep the exposure dose to a relevant range. While conditions in these tests are not typical, results do show that the uptake on the passive sampler is proportional to concentration and exposure time over a large dynamic range, and precisions comparable to other sampling methods are obtained. The following describes results of field tests aimed at demonstrating the real-life performance of both active and passive samplers.

Results – field study

Airborne VOC levels

Table 3 lists concentrations of the major VOCs measured in the printing area over four sampling days using active samplers (n = 20). This area had the highest concentrations in the facility (5-day average TVOC concentration of 52 mg m⁻³). VOC levels increased from morning to afternoon, and varied over a ~3-fold range from day-to-day, depending on activity and ventilation in the facility. During the winter study period with the windows and doors closed, the building had a high rate of air recirculation and low amount of outside air. This was reflected in VOC concentrations that varied slowly through the day and that were remarkably uniform throughout the non-office areas of the facility, as surveyed using a direct reading photoionization instrument.

Loading and breakthrough on active samples

The effect of sampling rate was examined using side-by-side samples in the press area taken at flow rates from 0.3 to 10.4 ml min⁻¹, giving sample volumes from 0.04 to 1.31. Flows below 10 ml min⁻¹ used the orifice to reduce diffusion errors. No systematic biases in VOC concentrations were observed, although some detection limit issues were noticed. For example, at the lowest sample volumes, low concentration compounds (<12 µg m⁻³), e.g., ethylbenzene, styrene, and naphthalene, were not consistently detected. Given the low flow rates, the sorbent tube sample would collect <0.5 ng of these compounds. High concentration VOCs were consistently detected. Loadings were not especially high in any of these
tests since the sample volume was very small. For example, at the highest concentration (98 mg m$^{-3}$), the total collected mass was only 24 mg with a sample volume of 0.24 l, or 127 mg for a 1.3 l sample, less than 2% of the maximum exposure in the laboratory test. In comparison, for ambient air measurements, we normally collect a 2 l sample, or up to 4 l if the relative humidity is low.8

Breakthrough of the adsorbent was examined using identical backup tubes with sampling rates from 0.3 to 10.4 ml min$^{-1}$. Excluding one compound (p-isopropyltoluene), the average concentration estimated on the backup tube was 12% of the total VOC concentration ($n$ ~ 52, 13 VOCs, 4 sets of tubes). A large portion of the breakthrough was due to contamination that occurred during handling of the tubes inside the facility, which resulted in exposure due to diffusion. (On subsequent days, tubes were prepared outside the facility, which greatly decreased blank errors.) As indicated, p-isopropyltoluene had significantly higher breakthrough (34% ± 10%) for reasons yet unknown. For all VOCs, sampling rate had no effect on the breakthrough fraction. Overall, breakthrough was not a concern in the case study.

Passive sampling

Fig. 4 compares results of the passive samplers to predictions based on the active sampling and the predicted uptake rates. As before, predictions are based on eqn. (4), VOC-specific diffusion coefficients, and concentrations measured using the active samplers. Predicted loadings were within a factor of two for all observed VOC concentrations except several 1,2,4-trimethylbenzene observations that just exceeded this limit. Good linearity and accuracy are seen between observed and predicted loadings ($r$ = 0.95). It should be noted that the passive samplers collected small quantities of VOCs. The largest loading, 780 ng, is 162 times lower than the corresponding active sample.

While the preceding analysis shows that the passive sampler gives linear responses over a wide range, field study results (Fig. 4) show somewhat more scatter than laboratory tests (Fig 2). The field study involves several sources of error beyond those discussed for the laboratory study, including slightly different sampling times and durations for each sample, temperature changes in the field, which would alter the diffusion rate, and possible blank contamination in some samples from exposure in the printing facility and during transit.

VOC emission sources in the field study were easily identified by the composition of materials used at the facility. Headspace measurements indicated that the major VOCs present in the solvent wash were xylenes, isopropylbenzene, propylbenzene, 1,3,5- and 1,2,4-trimethylbenzene (100 to 5,200 mg m$^{-3}$ for individual compounds, 8,000 mg m$^{-3}$ for total VOCs, all at 25 °C, Table 3). The principal compound was 1,2,4-trimethylbenzene, accounting for 66% of the total VOCs in the headspace. The wash also contained smaller amounts of n-hexane, toluene, ethylbenzene, sec-butylbenzene, and p-isopropyltoluene.

In comparison, VOCs emitted from the printing inks and varnishes were simpler mixtures consisting largely of 2-butanone, toluene and trace amounts of trimethylbenzene. The inks and varnishes were of high viscosity and low volatility, and although heated, headspace concentrations were low (3–63 mg m$^{-3}$ total VOCs at 37 °C).

A quantitative apportionment of the airborne levels to the various emission sources was derived using a 'receptor'

### Table 3 VOC concentrations in the printing area measured over 4 study days using active sorbent tube sampling

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mean/µg m$^{-3}$</th>
<th>Minimum/µg m$^{-3}$</th>
<th>Maximum/µg m$^{-3}$</th>
<th>Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>69</td>
<td>25</td>
<td>93</td>
<td>0.13</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>7</td>
<td>6</td>
<td>7</td>
<td>0.01</td>
</tr>
<tr>
<td>Benzene</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>0.00</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>15</td>
<td>7</td>
<td>7</td>
<td>0.03</td>
</tr>
<tr>
<td>Toluene</td>
<td>2,887</td>
<td>692</td>
<td>6,087</td>
<td>5.59</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>12</td>
<td>4</td>
<td>25</td>
<td>0.02</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>85</td>
<td>31</td>
<td>155</td>
<td>0.16</td>
</tr>
<tr>
<td>Styrene</td>
<td>3</td>
<td>1</td>
<td>5</td>
<td>0.01</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>604</td>
<td>245</td>
<td>1,156</td>
<td>1.17</td>
</tr>
<tr>
<td>Isopropylbenzene</td>
<td>399</td>
<td>164</td>
<td>776</td>
<td>0.77</td>
</tr>
<tr>
<td>Propylbenzene</td>
<td>3,804</td>
<td>1,515</td>
<td>7,418</td>
<td>7.37</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>7,792</td>
<td>2,941</td>
<td>15,109</td>
<td>15.09</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>35,274</td>
<td>15,129</td>
<td>66,714</td>
<td>68.31</td>
</tr>
<tr>
<td>sec-Butylbenzene</td>
<td>143</td>
<td>69</td>
<td>233</td>
<td>0.28</td>
</tr>
<tr>
<td>p-Isopropyltoluene</td>
<td>70</td>
<td>42</td>
<td>129</td>
<td>0.14</td>
</tr>
<tr>
<td>Limonene</td>
<td>786</td>
<td>182</td>
<td>1,096</td>
<td>1.52</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>5</td>
<td>1</td>
<td>7</td>
<td>0.01</td>
</tr>
<tr>
<td>Total</td>
<td>51,640</td>
<td>21,137</td>
<td>98,434</td>
<td>100.00</td>
</tr>
</tbody>
</table>

---

controls for printing facilities have been previously evaluated. These studies have shown a large variety of airborne contaminants associated with printing operations, including acetone, benzene, butoxyethanol, cumene, cyclohexanone, ethanol, ethoxyethanol, ethyl benzene, hexane, isobutanol, isopropanol, methanol, methylene chloride, methyl ethyl ketone, methyl isobutyl ketone, naphthalene, perchloro-ethylene, propyl alcohol, toluene, trichloroethane, trimethyl benzene, xylene. Additionally, polycyclic aromatic hydrocarbons, mostly 2 and 3 cycle compounds, have been measured in commercial printing facilities at relatively low levels (average of 16.5 μg m⁻³ including naphthalene). In this study, we found many of the same aromatic compounds, but relatively few chlorinated and oxygenated compounds, probably due to formulation changes over the years as well as the limited number of operations at the selected facility. Airborne levels did not exceed occupational standards.

Dynamic range

We have shown that thermal desorption tubes can be used in both passive and active sampling modes in various environments to identify and quantify target compounds over a very large sampling rate. For active sampling, flows from 10 to ~40 ml min⁻¹ can be used with the typical open tube configuration; flows from 0.5 to 10 ml min⁻¹ should use an orifice or other device to restrict diffusion that can bias results. Passive sampling achieves yet lower sampling rates, from 0.1 to 0.2 ml min⁻¹ using the orifice (depending on the specific VOC and temperature). Overall, the tested sampling rates spanned a 400-fold range. In the laboratory, the 10 min sample represented an exposure dose of ~40,000 ppm-min; the highest 2 h field samples represented a dose of ~6,000 ppm-min. These doses considerably extend the range of thermally-desorbed passive samplers found in the literature. Moreover, laboratory results suggest that the passive method can accommodate yet higher loadings and allow a working range reaching most 8 h TLVs, thus enabling use in the workplace.

The large dynamic range can present analytical challenges. For thermal desorption and GC-MS, adsorbent uptake of 1 ng (and often much less) is sufficient for compound identification and quantification. In laboratory and field tests, uptakes ranged to 5,700 ng for a single compound. At such loadings, instrumental limitations became apparent and a non-linear calibration was necessary to correct for diminished response of the MS. In air sampling, the use of flame ionization detection (FID) can give good results over a larger dynamic range than MS. Thus, the high loadings that would be expected in occupational applications might best be analyzed using FID. MS electron multipliers (EM) with a wider dynamic range.

Discussion

The high sensitivity of thermal desorption techniques, large selection of sampling rates enabled by using both active and passive samplers, and wide dynamic range of modern analytical instruments together could be much more extensively utilized for VOC sampling in occupational environments. In this paper, we have emphasized the development and evaluation of systems that sample at low rates, which permit great flexibility in designing sampling strategies, especially for the collection of long duration ‘integrated’ samples.

Field study results

The case study demonstrates sampler performance in a real-world setting involving complex mixtures. The commercial printing industry largely consists of small companies that use a variety of chemicals and work practices, thus results presented here are not necessarily representative of the industry. Because of their potential significance, exposures, emissions and controls for printing facilities have been previously evaluated. These studies have shown a large variety of airborne contaminants associated with printing operations, including acetone, benzene, butoxyethanol, cumene, cyclohexanone, ethanol, ethoxyethanol, ethyl benzene, hexane, isobutanol, isopropanol, methanol, methylene chloride, methyl ethyl ketone, methyl isobutyl ketone, naphthalene, perchloroethylene, propyl alcohol, toluene, trichloroethane, trimethyl benzene, xylene. Additionally, polycyclic aromatic hydrocarbons, mostly 2 and 3 cycle compounds, have been measured in commercial printing facilities at relatively low levels (average of 16.5 μg m⁻³ including naphthalene). In this study, we found many of the same aromatic compounds, but relatively few chlorinated and oxygenated compounds, probably due to formulation changes over the years as well as the limited number of operations at the selected facility. Airborne levels did not exceed occupational standards.

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range (2 to 3 times greater) are available, which would partially resolve nonlinearity issues.

**Breakthrough and water management**

Two additional factors that must be considered in developing a sampling strategy are breakthrough of VOCs and water management. The significance of these factors depends on the flow rates and the adsorbent used. At low flow rates, breakthrough is unlikely to pose problems in most applications if moderate to high capacity adsorbents are used, such as Tenax GR. This adsorbent is also hydrophobic, minimizing uptake of water. However, the dual bed sorbent tube included Carbosieve SIII, which does collect water. Previous work has shown that in humid environments, sample volumes with this adsorbent should be < 2 l to avoid chromatography problems resulting from excessive water. In active sampling at 0.5 ml min⁻¹, the lowest recommended, a 2 l sample corresponds to a sampling time of 67 h; a flow rate of 1.4 ml min⁻¹ would be suitable to collect 24 h samples. Low flow rates have the effect of reducing the kinetic rate constant K, in the Wheeler equation used to predict breakthrough times, which in turn is inversely related to breakthrough time. If the K dependence is proportional to the square root of the sampling rate, then a 0.5 ml min⁻¹ flow rate gives ~6 times the breakthrough time at a more typical sampling rate of 17 ml min⁻¹. This contributes to the large dynamic range found experimentally.

Water management is also important in passive sampling. Given water vapor’s relatively high diffusion coefficient, the water sampling rate is ~0.5 ml min⁻¹, roughly twice that of any target VOC. Applying the same 2 l limit discussed above gives a maximum sampling time of 67 h. This would apply if the primary adsorbent was Carbosieve. Since Tenax GR is more hydrophobic, sampling periods of up to a week might be reasonable with this adsorbent.

**Passive sampling**

As mentioned, uptake rates during diffusive sampling may decline with exposure time, especially when using weaker adsorbents such as Tenax GC. This results as the adsorbent layer nearest the tube opening becomes saturated with the adsorbate, thus resistance to mass transfer is not only provided by the stagnant air gap, but also by the transport through the adsorbent packing. All of the cited studies used a sampler geometry that gave sampling rates higher than the orifice/tube combination used here. We did not notice any systematic changes in uptake rates, possibly because the increased mass transfer resistance represented a smaller fraction of the initial resistance posed by the narrower and longer tubes used, the Tenax GR was a sufficiently strong sorbent that did not become saturated under the test conditions, or possibly because sampling times were too short. The tests conducted here cannot be considered a full validation of the method. Studies using charcoal-type adsorbents show that performance may suffer at high temperatures and high humidities, conditions not evaluated here. As just discussed, sampling time may affect uptake. Only relatively short periods were evaluated here.

Thermally desorbable passive samplers have many advantages. They offer increased sensitivity since essentially the whole sample is available for analysis; huge dynamic range; freedom from solvent use and contamination issues associated with chemical desorption; and more rapid sample turnaround. In addition, the devise itself is reusable and can be used in either active or passive mode. Adsorbents can be easily replaced for customized applications. Once collected, adsorbent samples have been shown to have good linearity, excellent stability in long-term storage tests, high recovery, and good precision.

**Sampling strategy**

The ability to use standard active sampling tubes at low flows and as passive samplers provides several new capabilities. It greatly extends the dynamic range, thus enabling the same instrumentation and similar methods to be used for ambient air and workplace sampling, a significant advantage increasing comparability of the results. If the concentration to be measured is unknown, or if the concentrations of the compounds present span a large range, two (or more) passive samplers with differently sized orifices might be co-located to obtain several sampling rates, further increasing the dynamic range. Finally, operation of passive samplers is simple and cost-effective.

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**References**
