Time-Weighted Average Sampling with Solid-Phase Microextraction Device: Implications for Enhanced Personal Exposure Monitoring to Airborne Pollutants

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The solid-phase microextraction (SPME) device is used as a time-weighted average (TWA) sampler for gas-phase analytes by retracting the coated fiber a known distance into its needle housing during the sampling period. Unlike in conventional spot sampling with SPME, the TWA sampling approach does not allow the analytes to reach equilibrium with the fiber coating, but rather they diffuse through the opening in the needle to the location of the sorbent. The amount of analytes accumulated over time gives the measurement of the average concentration to which the device was exposed to. Depending on the sorbent used as the sink, TWA sampling for various analytes is possible with times ranging from 15 min to at least 16 h. Both the poly(dimethylsiloxane) (PDMS) and poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) fiber coating phases were tested, with the latter employing on-fiber derivatization for reactive carbonyl compounds, e.g., formaldehyde. Described herein are the theoretical and practical considerations for using the SPME device as a TWA sampler.

It is often necessary to describe the average analyte concentration over a long period of time, such as 8 h. To achieve this, two approaches are possible.[1] One way is to average the concentrations of a large number of grab samples, which were acquired at selected time intervals, for the total time of interest (eq 1). where

$$\bar{C}_{t_n} = \frac{C_1 t_1 + C_2 t_2 + C_3 t_3 + ... C_n t_n}{t_1 + t_2 + t_3 + ... t_n} \qquad (1)$$

$\bar{C}_t$ is the time-weighted average (TWA) concentration, C_1 is the analyte concentration observed for time t_1, and so on, until time t_n. The alternate approach to obtaining a TWA concentration is with one sample, except with this approach $t_1 = t_n$ (eq 1). In this case, the one sampler mass loads analyte in direct proportion to the bulk analyte concentration for the specific sampling period. Therefore, determining TWA concentrations this way is much simpler because of the smaller number of samples, which, in turn, minimizes the number of analyses.

There are two general strategies to TWA sampling with one sampler: that with *active* or that with *diffusive* sampling methods. Active sampling methods draw air suspected to contain the analytes of interest at constant flow rates over solid sorbents, into liquid absorbents, or into whole-air sampling devices.[1] TWA sampling with active methods possesses a number of difficulties. For example, costly air-sampling pumps and critical orifices, frequent calibration routines, and potentially faulty batteries tend to present constant hurdles to the air-sampling professional. In addition, except for thermally desorbed sorbent beds, sorbent beds in most of the cases cannot be reused and can require chemical desorption with toxic eluants.

Alternatively, *diffusive* sampling methods, first introduced some time ago,[2] obviate the need for air-sampling pumps, thus simplifying the overall sampling process. In addition, diffusive samplers are not affected by ambient pressure and temperature changes during sampling,[3,4] unlike that which is observed for sampling through critical orifices; however, the currently available diffusive sampling devices are also generaly costly, are not reusable, and maintain the use of toxic eluants. Furthermore, no analytical benefits are realized with their use. Another problem is that the background noise from these devices is extensive, as a result of their plastic components,[5,6] thus typically rendering them unusable for indoor-air and ambient-air measurements. What is required is a diffusive sampling system that does not suffer from these problems. The solid-phase microextraction (SPME) device is shown herein to be a viable diffusive sampling system for a broad range of analytes, without the drawbacks observed with conventional diffusive sampling systems.

Since its inception, SPME has been used to sample a considerable number of waterborne and airborne analytes.[7] At the heart

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Figure 1. A typical, open-faced, diffusive sampler with fixed path length (Z).

Figure 2. SPME device in the TWA sampling mode.

of the SPME sampler is a 1-cm-long fused-silica core, or polymeric core, coated with different fixed polymeric phases. Currently, a number of commercial phases are available which include poly-(dimethylsiloxane) (PDMS) coatings and others such as PDMS/divinylbenzene (PDMS/DVB). With the latter, PDMS is used to support the DVB on the fused-silica rod. The PDMS coating is a nonporous, amorphous, polymeric phase while PDMS/DVB can be considered predominantly a porous, polymeric phase. Analyte uptake with PDMS is via a*bs*orption while it is a*d*sorptive for PDMS/DVB. Reproducibility, bias, and method detection limits with SPME have been shown to be better than with conventional sampling methods, for both water and air sampling. As shown herein, SPME, with the PDMS and PDMS/DVB fiber coatings, is a viable tool for the TWA sampling of hydrocarbons and formaldehyde. This new TWA sampler provides significant advantages over other methods, such as its low cost, reusability, portability, and ease of deployment. There is also a large selection of organic phases to sample a broad range of airborne analytes. This approach is equal in overall analytical sensitivity to currently available diffusive sampling methods because all of the sorbed analytes are introduced into the analytical instrument for quantitation rather than a small fraction of the extract. The development of such a sampler will certainly enhance the industrial hygienist's ability to describe personal exposure to airborne analytes. In addition, its automation for routine analyses should be readily achievable using commercially available SPME field sampling devices, or experimental ones,[7] with a dedicated autosampler. Therefore, more samples will be acquired. The resulting implications are that better data on personal exposure to airborne chemicals, due to larger sample sets, will enhance researcher's understanding of the relationship between observed health effects and analyte concentrations.

THEORY

Figure 1 presents a typical, commercially available diffusive sampler. The sampler consists of a sorbent positioned a distance Z from the opening of fixed area A. SPME can also be used as a TWA sampler; this is simply done by retracting the sorbent coating (into the needle housing) a known distance Z from the opening of fixed area A (Figure 2).

Three assumptions should be considered when diffusive sampling.[8-10] First, the analyte concentration in the bulk of the
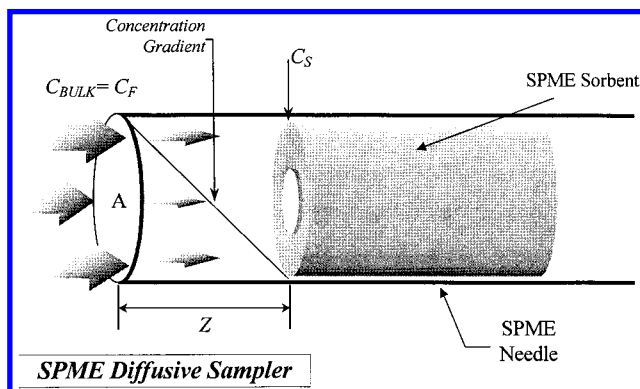
gas system, C_{BULK}, must equal the analyte concentration at the face of the sampling device, C_{FACE} (Figure 1). Second, the sampling device must respond in proportion to the changing analyte concentration at the face of the device. Third, the sorbent should be a "zero sink" for the target analytes, i.e., where the concentration of the analyte at the gas/sorbent interface for the sampling period is essentially zero, $C_S = 0$ (Figure 1). A zero sink ensures that once analyte is sorbed, that analyte does not alter the mass loading rate of additional incoming analyte.

Consider first the mass loading rate of an airborne analyte onto a sorbent with *active* sampling (eq 2). Here, the sampling rate, mass/time, depends on the sampling pump flow rate and the average analyte concentration Here M is the mass of analyte

$$\frac{M}{t} = R \times \bar{C} \tag{2}$$

sorbed, t is the sampling time, R is the pump sampling flow rate (vol/time), and $\bar{C}$ is the average analyte concentration (mass/vol) for the sampling time.

A similar description is possible with *diffusive* sampling devices.[7] From Fick's first law of diffusion (eq 3) where D is the

$$J = -D\left(\frac{dc}{dz}\right) \tag{3}$$

analyte diffusion coefficient (cm²/min), dc/dz is the analyte concentration gradient from the opening of the sampling device to the surface of the sorbent, and J describes the flux of analyte. Equation 3 can be modified to include the area (A) of the opening in the diffusive sampling device (eq 4, Figure 2): where dm is

$$\frac{dm}{Adt} = -D\frac{dc}{dz} \tag{4}$$

the weight of analyte passing through a cross-sectional area, A, (Figures 1 and 2) for a time dt. This amount is proportional to the linear-concentration gradient in the sampler (dc/dz) and the analyte diffusion coefficient D (cm²/min). For a given diffusive sampling device, such as that shown in Figure 2, area of opening,

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A, and the path length, Z (from eq 4), are constant; therefore, $dz = Z$ (eq 5 and Figure 2)

$$\frac{dm}{dt} = -\frac{DA}{Z}\,dc \qquad (5)$$

The product of D and A divided by Z dimensionally results in cm^3/min (R) (eq 6), although no air movement occurs

$$R = D\left(\frac{A}{Z}\right) \qquad (6)$$

Combining eqs 5 and 6 yields eq 7 where $\Delta C_{(S-F)}$ is the

$$\frac{dm}{dt} = -R\,dc = \Delta C_{(S-F)} \qquad (7)$$

gradient of analyte concentration between the face of the diffusive sampler and the sorbent. For an ideal sorbent[13] $\Delta C_{(S-F)} = -C_F$.

$$M = R\int_{t_1}^{t_2} C_F\,dt \qquad (8)$$

This expression describes the diffusive-sampler response under transient analyte concentrations as a function of time.[9,11,12,14] It is possible, however, to consider a simplified description recognizing that M/Rt will be an average sampling rate directly proportional to the average bulk analyte concentration over the time period from t_1 to t_2 (with $t_1 = 0$). Equation 9 can be realized for a steady-state analyte concentration at the face of the sampler.[6,9]

$$C_B = C_F = M/Rt \qquad (9)$$

Equation 9 indicates that the rate of analyte mass loading into the diffusive sampling device (M/t) is dependent on the sampling rate of the system (R) and is directly proportional to the bulk analyte concentration. It is recognized that R will be a constant for a given analyte and diffusive sampler and that it can be determined theoretically. It is sometimes difficult, though, to theoretically determine R, and so an empirical approach can be used (eq 10).[6,10,13,14]

$$K' = M/C_B t \qquad (10)$$

$K' = R$ according to this approach. Once K' is determined for an analyte with this device, it can be used to quantify unknown analyte concentrations by measuring the mass of analyte loaded, M, for a given sampling time, t. Therefore, unknown TWA concentrations can be determined by using this empirically determined constant.[10,15,16] It is in this way that the SPME sampling device can be practically used as a TWA sampler. For example, if the K' is known for a compound for TWA sampling with an SPME fiber coating, then quantification of its unknown concentration only requires a determination of the mass of compound on the fiber

for a given sampling time, t (eq 11), where M_f is the mass of

$$\frac{(M_f/t)}{K'} = \frac{M_f}{cm^3} = \bar{C}_B \qquad (11)$$

analyte measured on the fiber for a sampling time t (min) and K' is the empirically determined sampling rate constant, $K' = M_f/(\min \times ng/cm^3)$. Furthermore, as mentioned, one of the main advantages to using SPME as a TWA sampler is that the path length (Z) can be increased or decreased (Figure 2). This accommodates high concentrations or long sampling times, or when decreased, accommodates low concentrations or short sampling times (eq 12). Therefore, with a K' determined at L, moving the coating to path length L' proportionally changes the analyte-sampling rate. The effect of changing the path length from L to L' is shown (eq 12).

$$\bar{C}_B = \frac{(M_f L')/t}{K'L} \qquad (12)$$

Equation 12 indicates that if K' is determined at L and, if the sampling occurred at L', then a factor of L'/L is required to correctly describe the analyte $\bar{C}_B$. A factor greater than 1 is required when $L' > L$, one less than 1 is required when $L' < L$, and no factor is required when $L' = L$.

EXPERIMENTAL SECTION

Chemicals. Benzene, toluene, ethylbenzene, p-xylene, o-xylene, 1,3,5-trimethylbenzene (mesitylene), α-pinene, d-limonene, n-pentane, n-hexane, n-undecane, and o-(2,3,4,5,6-pentafluoro-benzyl)hydroxylamine (PFBHA) were from Sigma-Aldrich (Mississauga, Ontario). Carbon disulfide was from BDH (Toronto, Ontario). Formaldehyde (HCHO), 37% stabilized with methanol, was from Fisher Scientific (Nepean, Canada).

Materials. Nitrogen, helium, and hydrogen gases for flame-ionization detection and compressed air for standard-gas generation, as well as regulators for the compressed air were from Praxair (Waterloo, Ontario). Air for the flame ionization detector was generated from an air generator (Balston). All SPME fiber assemblies, syringes, diffusive badges, charcoal tubes, vials, and columns were from Supelco (Supelco, Canada).

Standard Gas Mixtures of Hydrocarbons and HCHO. Standard gas mixtures of hydrocarbons were prepared by properly mixing 0.75 g of each analyte. This liquid mixture, made up of 9.1% w/w of benzene, toluene, ethylbenzene, p-xylene, o-xylene, mesitylene, α-pinene, d-limonene, n-pentane, n-hexane, and n-undecane, was used in a liquid-injection/gas-dilution system to generate standard gas mixtures.[17] Here, a 500 μL Hamilton gastight syringe was used in the syringe pump to deliver the analyte mixture into a heated mixing tee with air flowing at 200 mL/min (25°). This concept has been used to generate ppmv concentration ranges of analyte.[18] With a 4.4 mg/h delivery rate,

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the individual analyte gas concentrations were 34 μg/L at NTP and were confirmed using a standard air sampling technique.[17] The SPME TWA sampling of these hydrocarbons occurred with the fiber retracted 3 mm from the needle opening ($Z = 3$ mm) (Figure 2). The path lengths were determined by inserting a wire with an outside diameter equal to the diameter of the fiber coating and measuring the distance to the tip of the fiber.

A commercially available standard-gas generator (model 491-B, Kin-Tek, Texas City, Texas) was used to generate all HCHO standard-gas concentrations. It was equipped with a mass flow controlled dilution gas system and temperature-controlled holding zone for the National Institute of Standards and Technology certified (NIST) HCHO permeation tubes from Kin-Tek. The use of permeation tubes for the preparation of primary standard-gas mixtures has been described.[19]

Instrumentation and Methods for SPME and Liquid Injections. A Varian Star computer controlled Varian 3400 *CX* gas chromatograph equipped with a carbon dioxide cooled septum-equipped programmable injector (SPI) was used for all experiments. A 0.8 mm i.d. SPI insert coupled to a SPB-5 column (30 m, 0.25 mm i.d., 1.0 μm film thickness) was coupled to a flame ionization detector (FID). The injector was maintained at 225 °C for SPME injections except for liquid injections where its initial temperature was 45 °C, which was then ramped to 225 °C at 30 °C/min. The column temperature program for SPME of hydrocarbons and liquid injections was 45 °C for 1.50 min, 30 °C/min to 175 °C held, for 2.67 min, then 30 °C/min to 240 °C, held for 2.0 min. The carrier-gas velocity was 40 cm/s at 45 °C for both SPME and liquid injections. Detector gas flow rates were set to 300 mL/min for air and 30 mL/min for nitrogen and hydrogen.

All HCHO experiments used a Varian Star computer controlled Varian 3400 gas chromatograph equipped with an SPI injector. The injector was maintained at 210 °C for SPME injections, but 70 °C for hexane liquid injections, and was then ramped to 250 °C at 300 °C/min. The column temperature program for SPME and hexane liquid injections was 45 °C for 1.00 min, 30 °C/min to 200 °C, then 50 °C/min to 290 °C, held for 4.0 min. The column head pressure was set to 26 psi hydrogen which resulted in a carrier-gas velocity of approximately 58 cm/s. Care should be taken to ensure that all connections are properly sealed when working with hydrogen as a carrier gas.

Both instruments were checked on a daily basis for calibration using a liquid midpoint calibration standard. Any deviations in area counts greater than 15% required reinjection of that standard, and, if still greater than 15%, the instrument was recalibrated with a six-point calibration curve. In addition, quality of peak shapes, resolution, and retention times were carefully monitored to ensure all chromatography was within all required specifications.

Field Sampling with SPME Using PDMS. Charcoal tubes for active sampling, charcoal diffusive badge monitors, a portable photoionization detector (PID) (which employed active air sampling), and the SPME 100-μm PDMS were all used in this study. The sampling and analysis method for the tubes and badge monitors was NIOSH method 1501 (sampling at 100 mL/min for the tubes). The real-time gas detector used was a RAE portable PID set to 10.6 eV for nonhalogenated compounds, and it was calibrated the day before the study with a 100 ppm$_v$ standard of
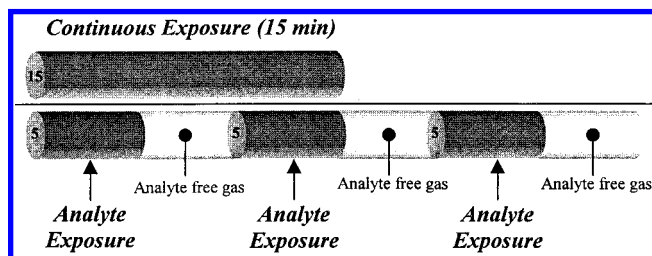

Figure 3. Continuous (15 min) and intermittent (15 min total) retracted-fiber exposure to the standard-gas mixture with a total of 15 min exposure to analyte-free gas.

isobutylene at 296 K and certified by the supplier of the equipment. For SPME with PDMS, eight 100-μm PDMS fibers were each conditioned at 250 °C for 1 h, then retracted and capped with a silicone septum. Three of the fibers were used for fast-grab sampling concurrent to active sampling with charcoal tubes, three were used for testing the viability of integrated sampling, and the last two were used as a field blank and a trip blank. For fast-grab sampling, the fibers were exposed to the test air for 5 min which was the same amount of time used for the active sampling on charcoal tubes. For TWA sampling, the fibers were left retracted in the assembly and exposed to the air for 30 min. Immediately after sampling with SPME with PDMS, all of the fibers were removed from the fiber holder and retracted approximately 1.5 cm into the barrel of its assembly. This was followed by capping the end with a new and clean 6-mm silicone septum then placing on a bed of dry ice along with the charcoal tubes. All SPME with PDMS and active charcoal tube samples were analyzed within 3 h of acquisition. The sampling temperature was 296 K and relative humidity was 25% during the sampling period.

Loading SPME Fibers with PFBHA. A solution of PFBHA·HCl (17 mg/mL) in formaldehyde-free water was placed in 4-mL amber Teflon capped vials, each with a 1-cm stir bar.[20] Various SPME fibers were placed in the headspace of the stirred solution (1800 rpm), immediately above the center of the vortex, for various times.

TWA Sampling with the PDMS/DVB Fiber Coating and On-Fiber Derivatization. The TWA sampling of formaldehyde with on-fiber derivatization employed standard-gas concentrations of formaldehyde from a system previously described.[20] Here, retracted-fiber exposure times ranged from 5 min to 16 h.

RESULTS AND DISCUSSION

Two types of TWA sampling with the SPME device are presented: sampling of hydrocarbons with 100-μm PDMS fiber coatings and on-fiber derivatization of HCHO using PFBHA doped PDMS/DVB fibers. Both theoretical and empirical uptake rates are compared for the former.

TWA Sampling with 100-μm PDMS Fiber Coatings: Hydrocarbons. The empirical and theoretical TWA sampling of hydrocarbons, each at 34 μg/L (25 °C), with 100-μm PDMS fiber coatings are presented. An empirical approach was used which was based on intermittent and continuous exposure to the test gases. The concept is that a strong sorbent will retain the analytes during the time when analyte concentrations vary from high to low. Figure 3 presents the retracted-fiber exposure patterns for

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both continuous- and intermittent-exposure routines to the standard-gas mixtures. For continuous exposure, the retracted fiber is continuously exposed to the standard gas for 15 min. For intermittent exposures, the retracted fiber is exposed to the standard gas for 5 min, then to analyte free gas for 5 min, and then to the standard gas, etc., for a 15-min total exposure time with a 15-min exposure to analyte-free gas. Therefore, the mass of each analyte on the sorbent should be the same for each exposure routine, and if taken as a ratio, should be 1, as was observed for some of the target analytes. The results from this study are presented in Figure 4. Here, the percent of analyte on the fiber from a 15-min intermittent exposure is presented relative to a continuous 15-min exposure cycle. The data in Figure 4 (solid columns) indicate (as expected) the ratios are less than 1 for those compounds with a low affinity for the coating, but approach 1 for analytes with increasing coating affinity. The compound's affinity for the PDMS fiber can be described with a distribution coefficient for the gas-phase analyte concentration to the fiber coating, K_{fg}. Previous work has indicated that the log K_{fg} is linearly related to carbon number for a series of hydrocarbons.[21] With increasing K_{fg}, there is an associated increase in the compound affinity for the PDMS coating. Therefore, as the K_{fg} increases, smaller analyte losses are expected from the coating during the time the fiber is exposed to the analyte-free gas, and it can be stated that the viability of TWA sampling with PDMS increases with increasing analyte affinity for the coating. The data show that 19% of n-pentanes desorb from the PDMS fiber coating during the nonexposure period while at the same time only 2% of n-undecane desorbs. If a 10% loss of analyte were tolerable for the sampling period, then the cutoff for TWA sampling with the 100-μm PDMS would start with toluene. This suggests that short-term TWA sampling, i.e., less than 30 min, should be possible with the 100-μm PDMS fiber coating for compounds with $K_{fg} > 1000$ and could be, more than likely, extended with larger PDMS coating volumes and/or by decreasing the sorbent temperature during sampling. This also suggests a method is available to discern which analytes are best long-term sampled by retracted sampling with 100-μm PDMS. A method to estimate K_{fg} from chromatographic parameters has already been presented.[21]

Figure 4 also presents the percent of analyte on the fiber for a continuous 15-min retracted-fiber exposure relative to the amount of analyte which was mass loaded at equilibrium (out of the needle sampling, lightly shaded columns).[7] The data indicate that those compounds with lower diffusion coefficients, and higher affinity, mass load only to a few percent of the equilibrium amount. Typically, no more than approximately 5% of equilibrium for an analyte mass loaded during TWA sampling can be tolerated before the amount of sorbed analyte begins to affect the mass-rate uptake of the diffusive-sampling device.[14] The data in Figure 4 indicate that n-pentane has reached 61% of the mass at equilibrium while n-undecane has only reached 0.8% for the 15-min sampling period. Therefore, if a limit of 5% of equilibrium is considered, it should be possible to TWA sample n-undecane for ~90 min with $Z = 0.3$ cm (15 min × 5% ÷ 0.8%) with this TWA sampling device without affecting its uptake rate. It is emphasized that this limitation does not outweigh the benefit to short-term TWA with the 100-μm PDMS coating.

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Table 1. Comparison of the Theoretical First Order Rate Uptake with the Experimentally Observed First Order Rate Constant[a]

	K' (pg/min × ppm$_v$)		TWA (% of theoretical)	
analyte	theoretical	empirical	15 min	0.25 min[b]
n-pentane	46	6	13	65
n-hexane	50	12	24	62
benzene	49	15	30	63
toluene	53	23	43	93
ethylbenzene	56	32	57	94
p-xylene	56	33	59	
o-xylene	56	35	62	
a-pinene	62	45	73	
mesitylene	59	44	73	
d-limonene	62	49	78	
n-undecane	66	64	96	

[a] 100-μm PDMS coating with a cross-sectional face area of 0.000 86 cm^2 and a 0.3-cm path length for dimensionless-gas concentration (ppm$_v$). [b] The last column presents the results from 15-s TWA sampling.

It should be recognized that if $C_S \neq 0$ (Figure 1) when TWA sampling with sorbents, then there is a vapor pressure of analyte above the surface of the sorbent which will reduce the tendency of additional analyte to proportionally mass load onto the sorbent. This presents a limitation to TWA sampling with PDMS as a sink, but also realizes a useful compromise in that those compounds with sufficiently large K_{fg} can be sampled in this way. It was found that those compounds with $K_{fg} > 3000$ can be TWA sampled (30 min) with the 100-μm PDMS coating because the mass-loading rates essentially remain proportional to the bulk analyte concentration for short sampling times, i.e., less than 30 min. This point is confirmed with the data for experimentally and theoretically determined K' values presented in Table 1 and with results obtained from a field study.

Table 1 summarizes the theoretical and experimentally observed first-order rate uptakes, obtained from 15-min continuous sampling for each analyte with the 100-μm PDMS. The data indicate there is increasing agreement between the experimental and theoretical K' with increasing K_{fg}, i.e., increasing analyte affinity for the coating. Furthermore, the agreement between theoretical and experimental K' values increases with decreasing retracted-fiber exposure times (Table 1), i.e., with 15-s TWA sampling (retracted-fiber position). The data indicate there is a substantially greater agreement between the theoretical and experimental K' for those compounds with a high affinity for the PDMS coating and for extremely short exposure times, the opposite being true for long exposure times, i.e., greater than 15 min. This suggests the viability of the TWA sampler with the PDMS coating for instantaneous measurements of such compounds. K' data for compounds after ethylbenzene could not be calculated due to the low mass loading with 15-s sampling. It is pointed out that the analyte diffusion coefficient, the area, A, and path length, Z, (Figure 2) control the analyte uptake rate into the diffusive sampler even though the sorbent at position Z does not occupy the same total cross-sectional area, as evidenced by the data in Table 1. If the cross-sectional area of the sorbent is used instead the sampler's, then a considerable underestimation of uptake is calculated.

It is recognized that a highly efficient sorbent will strongly retain sorbed analytes even when the sorbent is exposed to a gas
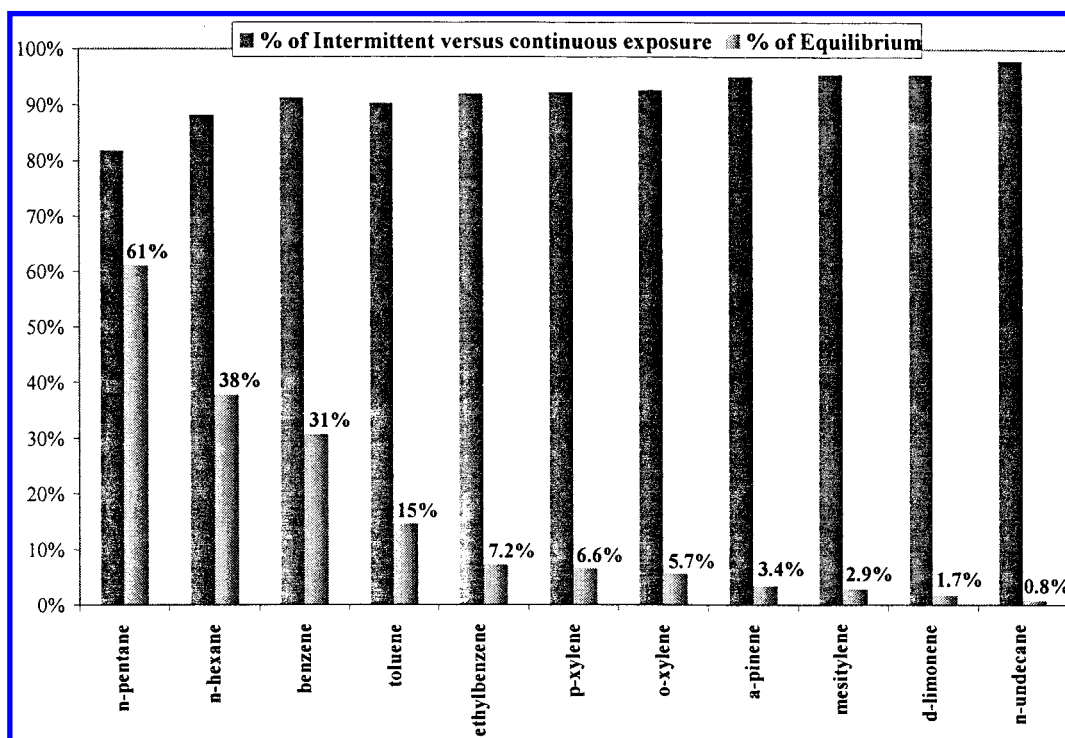
Figure 4. Relative amount of analytes on the 100-μm PDMS with intermittent exposure relative to continuous exposure. The shaded columns represent the percent of equilibrium reached for the continuous-15-min exposure.

with zero concentration of those analytes.[14] If, however, the sorbent does not strongly retain the analyte, then the sorbent may still be used for TWA sampling except only for short TWA sampling times, e.g., 15−30 min. Air samples acquired for these shorter integration times are often used to determine whether analyte concentrations have exceeded a short-term exposure limit.[1,22] Field-sampling styrene in an industrial facility demonstrated this point. Since the K_{fg} for styrene was experimentally determined to be approximately 3100,[21] little compromise to the overall accuracy was expected in TWA sampling with 100-μm PDMS. Charcoal tube samples (30 min) were used as the benchmark method and to this were compared data obtained by TWA sampling with the 100-μm PDMS fiber coating (3-mm retracted); concentrations of 54 μg/L (25 °C) versus 56 μg/L (25 °C), respectively, were determined.[17] These data indicate the tremendous promise of SPME as a TWA sampling device.

TWA Sampling Using On-Fiber Derivatization: HCHO. Perhaps the most ideal approach to TWA sampling with any diffusive sampler is to have the incoming target analyte derivatized to a stable product. Three general scenarios are possible with on-fiber or in-fiber derivatization, depending on the sorbent used and the rate of reaction between the analyte and the derivatization reagent.[7] The first scenario is that an incoming analyte sorbs then diffuses into the sorbent and slowly reacts with a derivatization reagent. The second scenario is that the incoming analyte sorbs then immediately reacts with a surface-borne derivatization reagent. The product of the reaction then diffuses into the coating, with an additional derivatization reagent diffusing back to the surface and reacting with additional incoming analyte.[7] The third scenario is with on-fiber reaction where incoming analyte reacts with surface-borne analyte and remains fixed at the site of reaction,

i.e., a surface-limited amount of derivatization reagent.[20] The third scenario was proven with the on-fiber derivatization of formaldehyde using PFBHA,[20] with the fiber in the retracted position, (Figure 2). Table 2A summarizes the exposure routines studied with this system. Four routines were tested with increasing complexity to study the effectiveness of on-fiber derivatization to act as the ideal zero sink. Table 2A presents the PFBHA/PDMS/ DVB fiber uptake of formaldehyde in the TWA sampling mode (moving from left to right for the exposure pattern). Note that all exposures were consecutive. Formaldehyde-free gas was used to test the viability of the sorbent to sustain binding of the product. This gas delivered over the fiber at the same velocity as that for the formaldehyde standard gas mixture. Each run was carried out in duplicate over a period of 3 days. The results from these findings are provided in Table 2B. The data indicate a cumulative amount of oxime is formed with intermittent fiber exposure to the formaldehyde standard gas, with no observable losses, thus proving the fact that this sampling system yields an ideal zero sink. For example, from Table 2B, essentially no losses were observed for a total sampling time of 60 min, where 30 min of the time the fiber sampled inside the sampling vessel and for the other 30 min the fiber sampled a formaldehyde-free gas stream (Run No. 4). In addition, the accumulated amount was directly proportional to the amounts obtained with different intermittent-sampling procedures.

The experimentally determined first-order rate constant, K', for this TWA sampling device was found to be 0.000348 ng/(s ppb$_v$) for $L = 0.3$ cm. With this K', the system was tested by exposing the fiber to 636 ppbv formaldehyde, with $L = 3.0$ cm, for 1007 min. The amount of PFBHA formaldehyde oxime formed after the exposure time was found to be 23.8 ng. Then, this amount as a function of time was divided by the K' obtained at $L = 0.3$

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(22) *Am. Conf. Gov. Ind. Hyg.*, TLVs and BEIs, 1996.

Table 2. Exposure Routines (A) and Summary of Data (B) for TWA Sampling

(A) TWA Sampling of HCHO (0.3-cm Retracted-Fiber L)

run no.	exposure routines						total sampling time (min)
1	E[a] (10 min)						10
2	E (30 min)						30
3	E (10 min)	NE[b] (10 min)	E (10 min)	NE (10 min)	E (10 min)	Ne (10 min)	60
4	E (30 min)	NE (30 min)					60
5	E (1007 min)						1007

(B) TWA Sampling of 636 ppb$_v$ Formaldehyde with PFBHA/PDMS/DVB Fibers

run no.	total exposure time (min) to HCHO (636 ppb$_v$)	total exposure time (min) to HCHO-free gas	ng (fiber)	Z (mm)	ng/min	K' ng/ppb$_v$ min/3.0 mm
1	10	0	2.2	3.0	0.22	0.000346
2	30	0	6.7	3.0	0.22	0.000351
3	30	30	6.7	3.0	0.22	0.000349
4	30	30	6.6	3.0	0.22	<u>0.000346</u>
					average K' →	0.000348

run no.	total exposure time (min) to HCHO (636 ppb$_v$)	total exposure time (min) to HCHO-free gas	ng (fiber)	Z (mm)	ng/min		% error (to 636 ppb$_v$ theoretical)
5	1007	0	23.8	30	0.024	679 ppb$_v$	6.8

[a] E, exposure to formaldehyde (636 ppb$_v$) (25 °C). [b] NE, no exposure to formaldehyde—exposed to gas with zero-concentration formaldehyde. [c] The run nos. are described in (A).

Table 3. Summary of Airborne (Industrial) Formaldehyde Concentrations (ppb$_v$) Comparing 420-min SPME TWA Sampling with On-Fiber Derivation and 420-min Active Air Sampling Using NIOSH Method 2541

SPME TWA (7 h)	standard method (TWA 7 h)
109	102
152	160
57	51

cm. Therefore, a multiplication factor of 10 was used, i.e., the ratio between the path lengths (eq 12). The result was that the actual concentration was within 7% of the expected formaldehyde concentration. This was repeated twice, and each time the findings were similar. These data indicate that both short- and long-term TWA sampling for formaldehyde is possible with SPME using PFBHA coated onto PDMS/DVB fibers. Since this is the same commercially available fiber used for grab sampling of formaldehyde discussed elsewhere,[20] it is now possible to do both grab sampling and TWA sampling of gaseous formaldehyde with the *same* sampling device.

This sampling system was field-tested against a standard reference method for airborne formaldehyde. TWA sampling with this SPME system was carried out with the fiber retracted to 3.0 cm, for a 420-min sampling period. These data are presented in Table 3. The data indicate that TWA sampling with SPME for formaldehyde presents no compromises compared to the results obtained from currently used, standard sampling methods.

CONCLUSIONS

The commercially available SPME device can be successfully used as a TWA diffusive sampler for both hydrocarbons and formaldehyde. The device is very flexible, is reusable, eliminates organic solvents, and the analytical process can be easily automated. It can be used for spot and/or TWA applications. One of the advantages of diffusive sampling with the SPME device over currently available alternatives is that the SPME sorbent can be moved to different path lengths, i.e., the distance from the opening to the sorbent face can be increased or decreased. Therefore, the same sampling device can be used for TWA sampling over a large range of analyte concentrations and/or at various sampling times, depending on mass-detection requirements. Also, the integration factor can be changed during a single measurement by varying the position of the fiber during the experiment. Another advantage is that this TWA sampling system is perfectly suited to the sampling and analysis of indoor air and ambient air analyte concentrations. This is due in part to the fact the SPME is housed in stainless-steel tubing during the sorption and desorption steps, which also provides protection from damage during sampling. All sorbed analytes are introduced to the analytical instrument for quantitation, which ensures high sensitivity. The sampler is cost-effective and has been further enhanced by commercially available field sampling holders and stronger sorbents, such as the Carboxen/PDMS coating. A rapid, yet accurate, method to determining the most suitable sorbent for TWA sampling with SPME can possibly be achieved by determining the heat-of-enthalpy change upon sorption of the analyte to the sorbent.[23] This would simplify the process of searching for highly efficient SPME sorbents.

New user-friendly device designs looking, for example, like pens would benefit acceptance of the technology. In-depth side-

(23) Stanetzek, I.; Giese, U.; Schuster, R. H.; Wunsch, G. *Am. Ind. Hyg. Assoc. J.* **1996**, *57*, 128−133.

by-side field and validation studies[24] are required with the ultimate goal of developing TWA using SPME into a standard method; active research in this area is under way in our laboratory. This principle of TWA is not limited to measurement in gaseous media. Similar approaches can be developed for liquid samples, such as water effluents.

(24) Kennedy, E. R.; Fischbach, T. J.; Song, R.; Eller, P. M.; Shulman, S. A. *Analyst* (Cambridge, U.K.) **1996**, *121*, 1163−1169.