

Air Sampling with Porous Solid-Phase Microextraction Fibers

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A new, rapid air sampling/sample preparation methodology was investigated using adsorptive solid-phase microextraction (SPME) fiber coatings and nonequilibrium conditions for volatile organic compounds (VOCs). This method is the fastest extraction technique for air sampling at typical airborne VOC concentrations. A theoretical model for the extraction was formulated based on the diffusion through the interface between the sampled (bulk) air and the SPME coating. Parameters that affect the extraction process including sampling time, air velocity, air temperature, and relative humidity were investigated with the porous (solid) PDMS/DVB and Carboxen/PDMS coatings. Very short sampling times from 5 s to 1 min were used to minimize the effects of competitive adsorption and to calibrate the extraction process in the initial linear extraction region. The predicted amounts of extracted mass compared well with the measured amounts of target VOCs. Findings presented in this study extend the existing fundamental knowledge related to sampling/sample preparation with SPME, thereby enabling the development of new sampling devices for the rapid sampling of air, headspace, water, and soil.

Solid-phase microextraction (SPME) presents many advantages over traditional analytical methods by combining sampling, preconcentration, and the transfer of the analytes into a standard gas chromatograph (GC).¹ To date, SPME has been successfully applied in numerous environmental, food, flavor, pheromone, pharmaceutical, clinical, and forensic applications.^{2,3} Several research studies have focused on the application of SPME to air sampling and analysis.^{4–6} SPME sampling methods have been developed for total volatile organic compounds (TVOCs), formaldehyde, and volatile organic sulfur compounds in air.^{7–10} SPME can also be used for time-weighted average (TWA) of airborne

VOCs.^{11,12} In addition, recent studies indicate that SPME can be used for sampling and analysis of aerosols and airborne particulate matter.^{13,14}

To date, the poly(dimethylsiloxane) (PDMS) coating is one of the most widely used coatings for extracting volatile analytes from environmental samples via absorption.^{1–3} The relative ease of the extraction process control and the fact that the absorption process is not affected by competition between the absorbed analytes prompted the development of air sampling methods based on the PDMS coating.^{7,8} In addition, the theory behind the equilibrium and nonequilibrium extraction process for absorptive (liquid-phase) PDMS coatings is well understood and described in the literature.^{1–3,15–17}

In contrast, the sensitivity of solid (or mixed-phase) SPME coatings, such as PDMS and divinylbenzene (PDMS/DVB) and Carboxen/PDMS, was reported to be much higher compared to PDMS for extracting VOCs.^{18–20} The PDMS/DVB coating can extract (via adsorption) greater amounts of VOCs than the PDMS coating, particularly when short sampling times and nonequilibrium conditions are used.²¹ However, competitive adsorption and displacement effects make mass calibration and quantification particularly challenging. Several attempts had been made to describe the extraction process with adsorptive SPME coatings. First, an equilibrium theory for analyte extraction into selected porous polymer fibers was developed.²⁰ Recently, the kinetics of a single-analyte adsorption and saturation of a thin SPME coating was described using the moving boundary model.²² However, such sampling conditions are rare in real air sampling where many analytes are usually present. Thus, other alternative approaches must be used to make the air sampling with solid coatings quantitative.

To take the full advantage of the high sensitivity of solid SPME coatings for air sampling, a new approach relying on diffusion-controlled extraction, described in this paper, should be used. It

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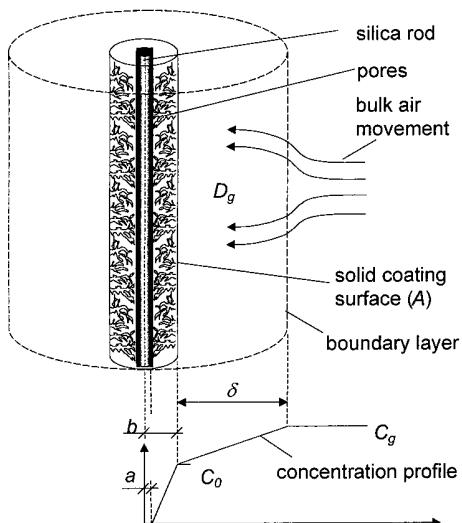


Figure 1. Schematic of rapid extraction with solid (porous) SPME fiber coating in a cross-flow. The extraction is described by eq 1.

was shown before that diffusion can control the extraction process in some cases of sampling with exposed absorptive coatings, e.g., perfect agitation conditions and very short sampling times.¹ In this research, the mass calibration and quantification for airborne VOCs with adsorptive coatings was based on the gas-phase molecular diffusion coefficient (D_g) for each analyte, the analyte concentration in the air, the sampling time, and the thickness of the boundary layer around the fiber coating. Very short sampling times and nonequilibrium conditions were used to minimize the effects of competitive adsorption and to calibrate the extraction process in the initial linear extraction region.

The objective of this research was to demonstrate the use of diffusion-controlled extraction for rapid air sampling of VOCs with solid SPME coatings under nonequilibrium conditions and to discuss and verify with experimental data the theory behind this technique. The effects of several parameters influencing the extraction process, optimization of rapid sampling with solid SPME fibers, the significance of this research to air sampling, the need for development of new sampling devices, and the potential of novel applications of diffusion-based extraction into fast sampling of water and other matrixes were also discussed.

THEORY

Extraction Model Development. The solid SPME fiber coating can be modeled as a long cylinder with length L and outside and inside diameters of b and a , respectively (Figure 1). When the coating is exposed to moving air, an interface (or boundary layer) with thickness δ develops between the bulk of air and the idealized surface of the fiber. The analytes are transported from the bulk air to the surface of the coating via molecular diffusion across the boundary layer. In most cases, the molecular diffusion of analytes across the interface is the rate-limiting step in the whole adsorption process.

The analyte concentration in the bulk air (C_g) can be considered constant when a short sampling time is used and there is a constant supply of an analyte via convection. These assumptions are true for most cases of SPME air sampling, where the volume of air is much greater than the volume of the interface and

the extraction process does not affect the bulk air concentration. In addition, the SPME solid coating can be treated as a perfect sink. The adsorption binding is instantaneous, and the analyte concentration on the coating surface (C_0) is far from saturation and can be assumed to be negligible for short sampling times and relatively low analyte concentrations in a typical air. These concentrations range from parts-per-trillion (by volume) to parts-per-million (by volume) for most VOCs of interest and typical industrial hygiene, indoor, and ambient air concentrations.²³ The analyte concentration profile can be assumed to be linear from C_g to C_0 . In addition, the initial analyte concentration on the coating surface (C_0) can be assumed to be equal to zero when extraction begins. Diffusion inside the pores of a solid coating controls mass transfer from b to a .

The mass of extracted analyte with sampling time can be derived using the analogy of heat transfer in a cylinder with inside and outside diameters of b and δ , respectively, with a constant axial supply of heat.²⁴ The steady-state solution to heat transfer can be translated into a mass-transfer solution by replacing temperatures with concentrations, heat with flux of mass, and heat-transfer coefficient with gas-phase molecular diffusion coefficient. As a result, the mass of extracted analyte can be estimated from the following equation:

$$n(t) = \frac{2\pi D_g L}{\ln((b + \delta)/b)} \int_0^t C_g(t) dt \quad (1)$$

where n is the mass of extracted analyte over sampling time (t) (ng), D_g is the gas-phase molecular diffusion coefficient (cm^2/s), b is the outside radius of the fiber coating (cm), L is the length of the coated rod (cm), δ is the thickness of the boundary layer surrounding the fiber coating (cm), and C_g is analyte concentration in the bulk air (ng/mL). It can be assumed that the analyte concentration is constant for very short sampling times and therefore eq 1 can be further reduced to

$$n(t) = \frac{2\pi D_g L}{\ln((b + \delta)/b)} C_g t \quad (2)$$

where t is the sampling time (s). The fiber length and the outside diameter of the fiber coating are constant for each type of the fiber.¹⁸ The nominal length for the 65- μm PDMS/DVB and the 75-mm Carboxen/PDMS coatings is $L = 1$ cm, and the outside diameter $2b = 0.0240$ cm ($\pm 10\%$) and $2b = 0.0260$ cm ($\pm 10\%$), respectively.¹⁸

It can be seen from eq 2 that the amount of extracted mass is proportional to the sampling time, D_g for each analyte, and bulk air concentration and inversely proportional to δ . This in turn allows for quantitative air analysis. Equation 2 can be modified to estimate the analyte concentration in the air (in ng/mL) for rapid sampling with solid SPME coatings:

$$C_g = \frac{n \ln((b + \delta)/b)}{2\pi D_g L t} \quad (3)$$

The amount of extracted analyte (n) can be estimated from the detector response.

For a special case, where the thickness of the boundary layer is much smaller than the outside radius of the fiber ($\delta \ll b$), the general solution can be reduced to a flat plate problem. For such condition, $\ln(1 + \delta/b) \approx \delta/b$, $2\pi bL = A$, and eq 2 simplifies to

$$n(t) = (D_g A/\delta) C_g t \quad (4)$$

where A is the surface area of the sorbent. Equation 4 is analogous to the mass uptake model for the TWA sampling with retracted SPME fiber, where the distance between the needle opening and the fiber (Z) is replaced by δ .^{11,12}

Under equal conditions, the amount of extracted mass will be greater for an analyte with a greater gas-phase molecular diffusion coefficient (D_g). This is consistent with the fact that the analyte with a greater D_g will cross the interface and reach the surface of the fiber coating faster. Values of D_g for each analyte can be found in the literature or estimated from physicochemical properties.²⁵ A number of methods have been proposed for estimation of diffusion coefficients of VOCs in air systems.^{25,26} The method by Fuller, Schettler, and Giddings (FSG) was reported to be the most accurate for nonpolar organic gases at low to moderate temperatures:²⁶

$$D_g = \frac{0.001 \times T^{1.75} \sqrt{1/M_{\text{air}} + 1/M_{\text{voc}}}}{p[(\sum V_{\text{air}})^{1/3} + (\sum V_{\text{voc}})^{1/3}]^2} \quad (5)$$

where D_g is expressed in cm^2/s , T is the absolute temperature (K), M_{air} and M_{voc} are molecular weights for air and VOC of interest, p is the absolute pressure (atm), and V_{air} and V_{voc} are the molar volumes of air and the VOC of interest (cm^3/mol). According to the FSG model, D_g is directly proportional to temperature and inversely proportional to air pressure. Because the atmospheric pressure changes are relatively low, the air temperature is a more important factor than pressure when considering air sampling. Regardless, both atmospheric pressure and air temperature are routinely monitored during conventional air sampling.

The thickness of the boundary layer (δ) is a function of sampling conditions. The most important factors affecting δ are SPME coating radius, air velocity, air temperature, and D_g for each analyte. The effective thickness of the boundary layer is determined by both rate of convection and diffusion. As the analyte approaches the sorbent surface, the overall flux is increasingly more dependent on diffusion than convection. The analyte flux in the bulk sample is assumed to be controlled by convection, whereas the analyte flux inside the boundary layer region is assumed to be controlled by diffusion. The effective thickness of the boundary layer can be described as the location where this transition occurs, i.e., where the flux toward δ (controlled by convection) is equal to the flux toward the surface of the SPME

coating (controlled by diffusion). In the Nernst model, the matrix within the boundary layer is stationary. Experimental research indicated that convection was also present inside the boundary layer. However, its effects decreased with the distance to the solid surface.²⁷ The effective thickness of the boundary layer can be estimated using eq 6, adapted from the heat-transfer theory for an SPME fiber in a cross-flow:¹

$$\delta = 9.52(b/Re^{0.62} Sc^{0.38}) \quad (6)$$

where Re is the Reynolds number = $2ub/v$, u is the linear air velocity (cm/s), v is the kinematic viscosity for air (cm^2/s), and Sc is the Schmidt number = v/D_g . The effective thickness of the boundary layer in eq 6 is a surrogate (or average) estimate and does not take into account changes of the thickness that may occur when the flow separates and/or a wake is formed. Equation 6 indicates that the thickness of the boundary layer will decrease with an increase of the linear air velocity (Figure 1). Similarly, when air temperature (T_g) increases, the kinematic viscosity also increases.²⁸ Since the kinematic viscosity term is present in the numerator of Re and in the denominator of Sc , the overall effect on δ is small.

The gas-phase molecular diffusion coefficient (D_g) for each analyte is also an important parameter controlling δ . As illustrated in eq 6, the effective thickness of the boundary layer will be reduced for analytes with lower D_g . This can be explained by considering that analytes with low molecular weight will reach the coating surface faster than the less volatile analytes under equal experimental conditions and therefore the point at which the diffusion is a primary mode of analyte transport to the coating is located further away from the surface. The reduction of the boundary layer and the increase of the mass-transfer rate for an analyte can be achieved in at least two ways, i.e., by increasing the air velocity and by increasing the air temperature. However, the temperature increase will reduce the solid sorbent efficiency. As a result, the sorbent coating may not behave as a zero sink for all analytes.

EXPERIMENTAL SECTION

Chemicals, Supplies, and Standard Gases. The volatile organic compounds under study (benzene, toluene, ethylbenzene, and *p*-xylene (BTEX)) were from Sigma-Aldrich (Mississauga, ON, Canada). National Institute of Standards and Technology (NIST) traceable certified permeation tubes for BTEX were from Kin-Tech (La Marque, TX). Ultrahigh-purity (UHP) hydrogen, helium, nitrogen, and air were from Praxair (Waterloo, ON, Canada). All SPME fibers and SPME holders were from Supelco (Oakville, ON, Canada). A standard gas-generating device with a flow-through sampling chamber was used to provide a wide range of target VOC concentrations at constant temperatures.¹³ This was accomplished by adjusting both the dilution air flow rate and the permeation tube incubating temperature.

Rapid Extraction: Effect of Air Velocity. A special air sampling system, consisting of a long glass cylinder with four different diameters (Glass Shop, University of Waterloo, ON,

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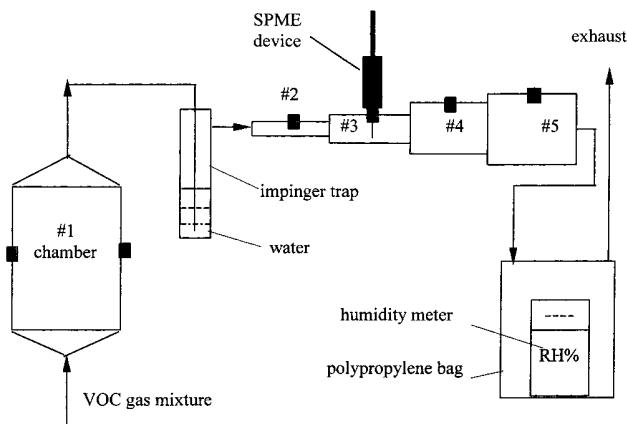


Figure 2. Schematic of the air sampling system for studying the effects of air velocity, air temperature, and relative humidity on adsorption with SPME fibers.

Canada), was constructed and installed downstream from the standard gas generator (Figure 2). The standard gas flow rate varied from 1000 to 4000 standard cubic centimeter per minute (sccm) to generating a wide range of air velocities at each diameter. Each section of the cylinder was equipped with sampling ports that were fitted with a half-hole Thermogreen septum (Supelco) for easy insertion of an SPME fiber for sample collection at a controlled air velocity. In addition, a 1-L glass sampling bulb (Supelco) was mounted downstream for static (no forced air flow) extractions.

The average air velocities were calculated by dividing the air flow rate by the cross-sectional area of each stage of the sampling cylinder (Figure 2). The average air velocities ranged from 0.2 to 83 cm/s, depending on the sampling port location, and the standard gas flow rate. The 65- μ m PDMS/DVB and the 75- μ m Carboxen/PDMS fiber coatings were used to sample the VOC gas mixture in each sampling port. Short exposure times ranging from 5 to 60 s were used to examine the effects of air velocity on the VOC adsorption process onto solid SPME coatings.

Rapid Extraction: Effect of Air Temperature and Relative Humidity. The air temperature in the main sampling chamber was varied from 22 to 40 °C, to study its effect on extractions with a 75- μ m Carboxen/PDMS and 65- μ m PDMS/DVB solid fiber coatings. The sampling times were 5 and 10 s, respectively. The air temperature in the vicinity of the SPME fibers was maintained within ± 0.3 °C. To create a dynamic air flow under different humidities, an in-line impinger trap (Supelco) and a digital humidity meter (Canadawide Scientific, Ottawa, ON, Canada) were installed (Figure 2). Relative humidities of 47 and 75% were obtained by maintaining the water level in the impinger trap at 1- and 8-cm height, respectively.

Gas Chromatography. A Varian 3400 GC (Varian, Sunnyvale, CA), equipped with a FID, was used to analyze air samples extracted by SPME fibers and liquid samples of standard compounds. A SPB-5 capillary column (30 m \times 0.25 mm i.d., 1.0- μ m film thickness) was installed in the GC and UHP helium was used as the carrier gas with a flow rate of 2 mL/min at 26 psi head pressure. The initial oven temperature was 50 °C for 1 min, followed by ramping at 15 °C/min to 240 °C, and maintained for 2 min. For SPME fiber desorption, the injector temperature was

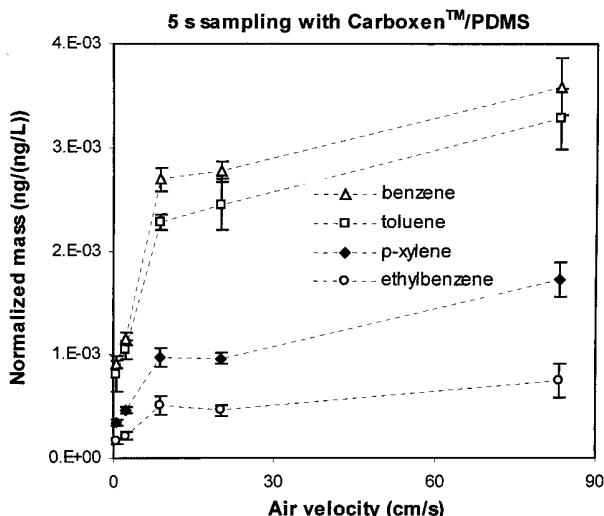


Figure 3. Effects of air velocity on the adsorption of BTEX onto the 75- μ m Carboxen/PDMS coating for 5-s sampling of standard gas mixture. Error bars signify ± 1 standard deviation from the mean of $n = 3$ samples.

set at 300 °C for Carboxen/PDMS fibers and at 250 °C for PDMS/DVB fibers. For liquid injections, the GC injector temperature was ramped from 45 to 225 °C at 300 °C/min. The quantification of target VOCs in standard gas mixtures was based on the response factors obtained from the FID response to liquid injections of VOC standards.

RESULTS AND DISCUSSION

Effects of Air Velocity. Extraction profiles for 5-s sampling of airborne BTEX with the 75- μ m Carboxen/PDMS coating were constructed for air velocities ranging from 0.2 to 83 cm/s (Figure 3). Each data point represents a normalized mass, i.e., the ratio of adsorbed mass and the analyte concentration in air, and is shown with ± 1 standard deviation for three samples. Figure 3 clearly indicates that two distinct regimes of mass transfer are present: regime 1, where the extracted amount depends on the air velocity, and regime 2, where the air velocity has a less significant effect on the amount of extracted mass ("semiplateau" region).

The two-zone phenomenon can be explained by considering an interface between air and the porous solid sorbent. The first region in Figure 3 describes diffusion of analytes through the static, well-developed boundary layer surrounding the SPME coating. In this region, the increase in air velocity causes a reduction in the boundary layer thickness and more of each analyte can be extracted per unit of time. This finding is consistent with the theory summarized by eq 2. In the second region, above some critical velocity, the thickness of the boundary layer is further reduced, but it is small enough that the mass transfer is controlled by the diffusion inside the pores of the SPME coating. Therefore, the increase in air velocity has only a small effect on the amount of extracted analyte.

The critical velocity for which the effects of the boundary layer thickness are negligible is ~ 10 cm/s for the analytes in this study. Although this range is lower than the average air velocities in ambient air, the critical velocity is close to the range of measured

air velocities in typical indoor air.²⁹ Reported average indoor air velocities at the breathing-zone height varied from 9.9 to 35.5 cm/s, with the average of 19 locations in a workroom varying from 1.4 to 9.7 cm/s.²⁹ Particular care must be taken to ensure the reproducibility of extraction conditions with porous SPME fibers in field sampling. This is because a small change in air velocity in the vicinity of solid SPME fiber can have a significant effect on the amount of adsorbed analyte, particularly in the first mass-transfer region (Figure 3).

Considering the fact that the amount of extracted mass for solid SPME fibers can be enhanced when sampling is conducted at greater air velocities, i.e., in the "semiplateau" region (Figure 3), an external fan or an attachment to an air sampling pump can be used to provide greater rate of mass transfer. Such a device could be used by air sampling professionals wishing to equalize the extraction conditions and provide reproducible effective thickness of the boundary layer for each sample. The use of a higher air velocity for sampling with solid SPME coatings leads to enhanced sensitivity. Preliminary results indicate that the use of solid PDMS/DVB 65- μm fiber coating, 30-s sampling, and average air velocity of 1 m/s allows for detection of BTEX at 10 ppt (by volume) range.³⁰

The greatest amount of mass was adsorbed for benzene, followed by toluene, *p*-xylene, and ethylbenzene. This finding is consistent with theory presented in eq 2; i.e., the mass of adsorbed analyte using rapid sampling is proportional to the D_g for each analyte, when all other sampling conditions are equal. The 75- μm Carboxen/PDMS coating was acting as a zero sink for short sampling times. The ratio of normalized masses in Figure 3 for benzene and toluene was close to the ratio of their D_g 's estimated by the FSG method.²⁶ Normalized masses for ethylbenzene and *p*-xylene were smaller than expected. This discrepancy is likely associated with experimental errors.

Verification of Theoretical Model. Good agreement between measured and predicted (using eq 2) amounts of extracted BTEX for rapid air sampling with the 65- μm PDMS/DVB coating was found. Figure 4 (part A) presents a comparison of measured and predicted mass of BTEX for air velocities of 0.8, 2.5, and 8.7 cm/s and sampling times of 5, 10, 20, 40, and 60 s. These air velocities were selected for the first mass-transfer region in Figure 3. For toluene, sampling times of 40 and 60 s were not included, because it was observed that the coating did not behave as a zero sink and the uptake was not linear with sampling time. For the same reason, data points for 30-, 40-, and 60-s sampling time were excluded for benzene. Theoretical concentrations were 356, 254, 77, and 140 ppb (by volume) for benzene, toluene, ethylbenzene, and *p*-xylene, respectively. The estimated (by eq 6) effective boundary layer thickness ranged from 3.4 to 0.74 mm for air velocities increasing from 0.8 to 8.7 cm/s. The latter velocity was very close to the threshold velocity of \sim 10 cm/s. The effective boundary layer thickness at the threshold is \sim 1 order of magnitude greater than the coating thickness, which indicates that the resistance to mass transfer in the coating (pores) becomes a significant factor in overall mass transfer in the system. The resistance to the mass transfer in the coating is controlled by coating porosity.

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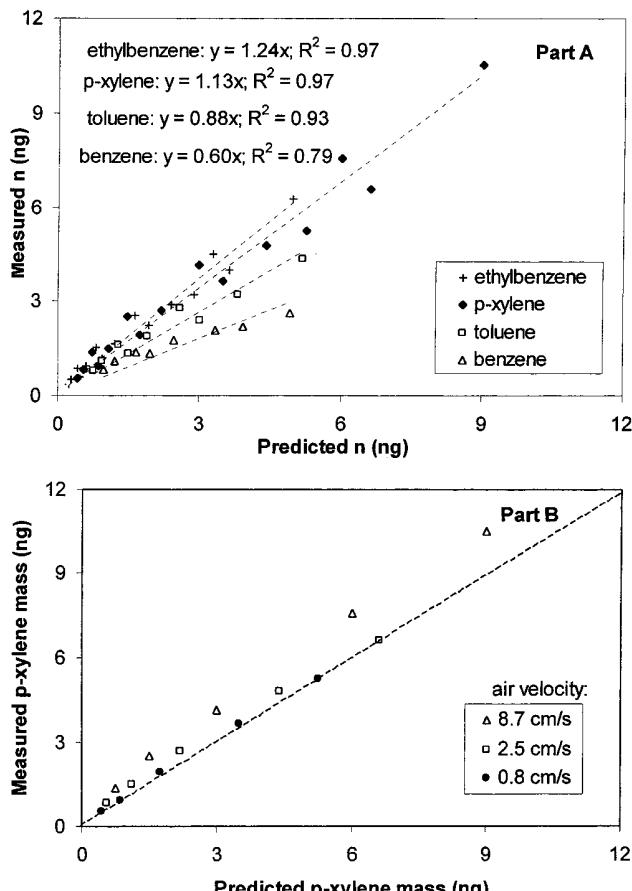


Figure 4. Comparison of measured and predicted (using eq 2) mass of adsorbed BTEX for rapid air sampling using the 65- μm PDMS/DVB coating (part A). Part B presents data for *p*-xylene only at various air velocities. Relative differences between $n = 2$ samples ranged from 0.0 to 14.4%, with the average of 2.4, 2.4, 3.6, and 3.5% for benzene, toluene, ethylbenzene, and *p*-xylene, respectively.

The slopes of the extraction data were close to the ideal value of 1 for *p*-xylene, ethylbenzene, and toluene. The largest discrepancy for the slope of extraction was found for benzene; i.e., slope = 0.60. The difference was lower for shorter sampling times. A similar trend was also found for toluene. This finding confirmed that the PDMS/DVB coating behaves as a zero sink for very volatile organic compounds only at very short sampling times. The coating behavior was much closer to the ideal zero sink for less volatile analytes (Figure 4, part B). The linear correlation coefficients were adequate for all analytes with the exception of benzene; i.e., $R^2 = 0.79$. The assumption of zero sink is valid for the Carboxen/PDMS coating, which has much greater affinity for highly volatile analytes.

Data presented in Figure 4 suggest that the slopes of extraction data were related to the gas-phase molecular diffusion coefficient (D_g) for each analyte. This is likely caused by the uncertainties associated with the semiempirical coefficients in eq 6, particularly with the weight assigned to D_g . Thus, the semiempirical eq 6 should be adjusted by assigning greater weight to the Schmidt number, to reflect the importance of D_g for accurate δ estimation.

No data points associated with the semiplateau region were presented in Figure 4. The semiplateau region refers to the high air velocity region, where the effective thickness of the boundary

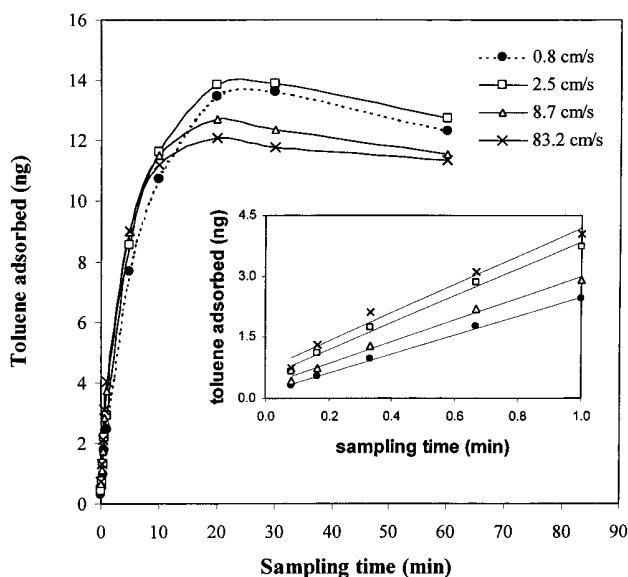


Figure 5. Extraction time profiles of toluene for different air velocities using the 65- μm PDMS/DVB fiber coating at 250 ppb (by volume). Relative differences between $n = 2$ samples ranged from 0.1 to 9%, with an average of 2.1%.

layer is reduced and the increase of air velocity has a lesser effect on mass transfer (Figure 3). In this region, the use of eq 2 results in overestimation of extracted mass by a factor of 2–10. Thus, eq 2 is applicable in the first mass-transfer region where the air velocities are relatively low, i.e., lower than ~ 10 cm/s, and the rate of extraction process is controlled by the thickness of the boundary layer. For velocities above this value, the calibration equation can be developed by considering properties of the fiber coating. The other option is to apply external calibration.

It is possible to obtain linear calibration curves with the 65- μm PDMS/DVB and the 75- μm Carboxen/PDMS coatings with rapid sampling. Figure 5 shows the extraction profiles for toluene using the 65- μm PDMS/DVB coating and different air velocities ranging from 0.8 to 83.2 cm/s. These curves illustrate the uptake of toluene for sampling time ranging from 5 s to 1 h. Toluene mass loading on the PDMS/DVB fiber coating increased linearly within a short, initial 1 min. Within this initial period, the toluene uptake rate was greater for higher air velocities (inset in Figure 5). The increase of air velocity reduced the thickness of the boundary layer and caused the increase of the amount of extracted toluene per unit of time. As the sampling time increased, the rate of extraction was also decreased until the amount of extracted mass reached a local maximum. The decrease of adsorbed toluene mass with time after the adsorption maximum indicates that competition and displacement of toluene by ethylbenzene and *p*-xylene (that were also present in the standard gas mixture) occurred. The local maximum of adsorbed toluene was lower and occurred faster for higher air velocity. This can be explained by considering the fact that the thickness of the boundary layer is smaller and the adsorption process is even more competitive at higher air velocities. As a result, the loading of ethylbenzene and *p*-xylene was also faster than at lower air velocities. This in turn, resulted in a lower amount of toluene adsorbed. Although not explicitly shown in Figure 5, the extraction curves for all velocities should merge at the sorption equilibrium.

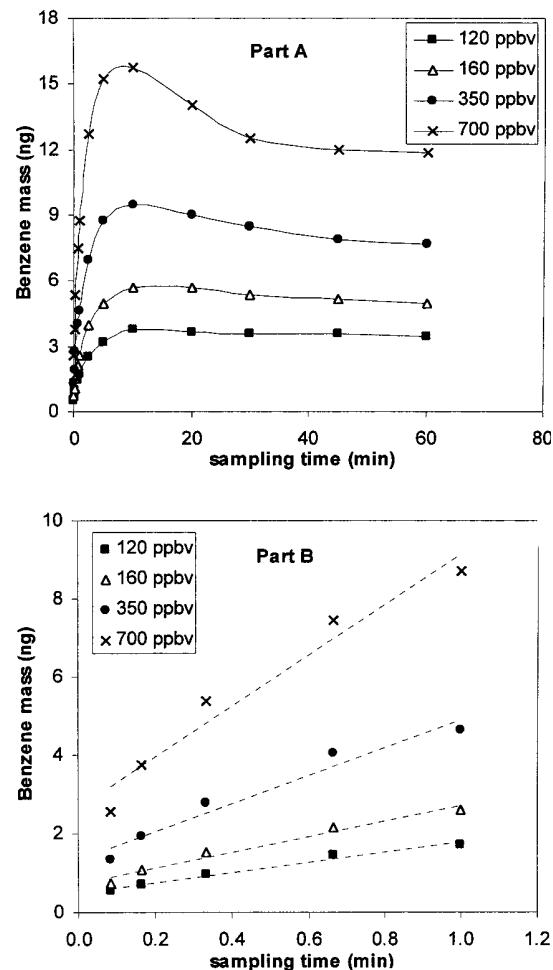


Figure 6. Extraction time profiles of benzene in a standard VOC mixture using a 65- μm PDMS/DVB fiber and average velocities equal to 10.2 cm/s (for 120, 160, and 350 ppb (by volume)) and equal to 20.4 cm/s for 700 ppb (by volume) concentration. Relative differences between $n = 2$ samples ranged from 0.0 to 17%, with an average of 1.9%.

Amount Adsorbed vs Analyte Concentration. Extraction profiles for all VOCs used in this study had a similar pattern for several standard gas concentrations. Figure 6 (part A) shows extraction profiles for benzene at four different concentrations ranging from 120 to 700 ppb (by volume) and sampling times ranging from 5 s to 60 min. In this case, the average air velocity was equal to 10.2 cm/s for 120, 160, and 350 ppb (by volume) concentrations and was equal to 20.4 cm/s for 700 ppb (by volume) concentration. As with toluene (Figure 5), the benzene uptake increased with the sampling time before reaching its equilibrium level. The rate of extraction and the extraction profile were dependent on benzene concentration. More mass per unit of time was adsorbed when extractions were conducted at greater concentrations, and the sorption equilibrium was reached in shorter time.

The decrease in adsorbed benzene mass with time after the adsorption maximum indicates that competition and displacement of benzene by toluene, ethylbenzene, and *p*-xylene took place. This effect was significant for higher analyte concentrations, i.e., 350 and 700 ppb (by volume). Figure 6 (part A) indicates that the PDMS/DVB fiber has a limited capacity of ~ 9 ng for benzene.

The saturation effects for benzene will be significant if the mass loading is greater than 9 ng. The total capacity of the fiber coating is approximately 30–40 ng, considering that there were four components of the standard gas present during extraction with concentrations similar to those of benzene. Thus, saturation effects will be significant if the total adsorbed mass is greater than 30–40 ng. It can be assumed that the PDMS/DVB coating can be considered a zero sink for rapid extractions, in cases where the total adsorbed mass does not exceed 30–40 ng for analytes with high affinity to the coating.

Mass calibration with the 65- μm PDMS/DVB fiber coating is also possible for rapid sampling conditions (Figure 6, part B). For a very short sampling time (less than 1 min), benzene mass loading was approximately linear with sampling time. Close evaluation of data suggested that the amount of adsorbed mass was a function of sampling time and analyte concentration. Extraction profiles were linear (or semilinear) only for rapid air sampling, i.e., when the sampling time did not exceed 1 min for all of the VOCs studied. Coating saturation occurred earlier for VOCs with lower molecular weight. These effects were negligible for low VOC concentration and were increasingly visible for higher concentrations. The linear correlation coefficient (R^2) improved from 0.95 to 0.99, for a benzene concentration decreasing from 700 to 120 ppb (by volume) and a sampling time up to 1 min. Furthermore, the linearity of the extraction was improved only if the first few data points were included, i.e., 5, 10, and 20 s. This was due to the fact that the coating did not behave as a zero sink for benzene and longer sampling times. The trend of improved linearity of the extraction profile with lower concentrations was also true for other VOCs in this study. However, the effect of coating saturation was becoming significant for longer sampling times compared with those associated with benzene.

The appropriate sampling time can be quickly estimated in the field by collecting and analyzing several air samples and observing the linearity of the extraction curve. In general, sampling time should not exceed 1 min when the rapid sampling methodology is used for VOCs. The sampling time should be further reduced if the target analytes have lower molecular weight than benzene, because smaller molecules will be extracted faster, if the affinities to the coating are comparable. Particular care should be exercised when concentrations of target analytes are near or greater than 1 ppm (by volume) range. In such cases, the sampling time should also be lower than 1 min. Similarly, lower than 1-min sampling should be used when a very complex matrix is sampled using rapid air sampling methodology. In such cases, the extraction may be more competitive, leading to displacement of analytes with low molecular weight.

Effect of Air Temperature. Comparison of typical extraction curves using the 75- μm Carboxen/PDMS/DVB fiber coating for 5- and 10-s sampling times at air temperatures ranging from 22 to 40 °C is presented in Figure 7 (part A). As expected, the amounts of extracted VOCs increased with exposure time. In all cases, the amount of extracted mass increased almost linearly when the air temperature increased from 22 to \sim 25 °C. This is due to the fact that D_g increases with temperature as predicted by eq 5. Similarly, the increase in temperature reduced n and subsequently δ as predicted by eq 6. Consequently, the rate of adsorption was raised as predicted by eq 2.

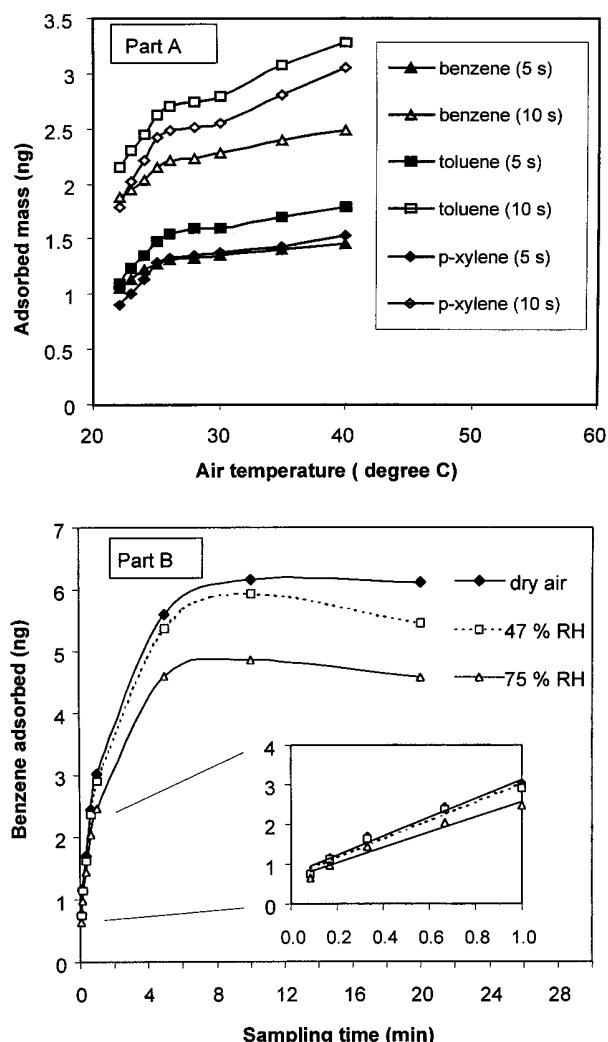


Figure 7. Temperature effect on VOC adsorption onto 75- μm Carboxen/PDMS fiber for 5- and 10-s sampling. Standard gas concentrations were 1380, 650, 300, and 400 ppb (by volume). Average relative differences between $n = 2$ samples were 1.1, 4.8, 5.0, and 3.6% for benzene, toluene, ethylbenzene, and *p*-xylene, respectively (part A). Part B illustrates extraction time profile for benzene at 240 ppb (by volume) and 65- μm PDMS/DVB at varying relative humidities. Average relative differences between $n = 2$ samples was equal 1.9%.

The shape of the extraction curves for the 65- μm PDMS/DVB coating and the 75- μm Carboxen/PDMS was similar in the initial temperature range from 22 to \sim 25 °C. Thus, the adsorption on the 65- μm PDMS/DVB coating was also diffusion-driven for very short sampling time and limited temperature range. However, the effects of sorbent saturation were very strong and dominating for very volatile analytes, particularly when longer sampling times, higher concentrations, or higher temperatures were used. As the temperature increased above 25 °C, the amounts of toluene and *p*-xylene adsorbed by the 65- μm PDMS/DVB increased slightly, while the amount of benzene adsorbed actually decreased. This can be explained by considering the reduction of sorbent effectiveness with temperature for more volatile analytes. For temperatures greater than 25 °C, the Carboxen/PDMS fiber coating was more efficient than the PDMS/DVB coating. The Carboxen/PDMS fiber

was also more efficient in extracting benzene and toluene, due to a higher affinity for both analytes to the coating.

Air (or extraction) temperature was recognized as one of the most important parameters in SPME sampling with liquid (or absorptive) coatings.^{5,8} The increase of the extracted amount with the increase of temperature for solid SPME fibers is an important finding that could be used as an optimization tool for rapid extractions. This finding is in agreement with the diffusion theory that predicts D_g -controlled extraction on a porous SPME fiber. The increase in air temperature increases the D_g for VOCs (eq 5). This in turn, causes the increase of adsorbed mass per unit time (eq 2). In contrast, when a pure-phase liquid SPME fiber is used, an increase in extraction temperature usually causes enhanced headspace extraction and simultaneously decreases the fiber coating/sample distribution constant.¹ Since the extraction by the SPME coating is an exothermic process, a decrease in mass loading at equilibrium is usually expected as the extraction temperature increases.

Effect of Humidity. Figure 7 (part B) presents the extraction time profiles of benzene using a 65- μm PDMS/DVB fiber coating to extract a standard VOC gas mixture at different relative humidities (RH). In general, the presence of humidity had a negative effect on the amount of VOCs adsorbed; i.e., less mass was adsorbed with greater RH level. The extraction profiles for toluene, ethylbenzene, and *p*xylene showed a similar trend. Water molecules competed with other VOC molecules and occupied a portion of active surface sites on the coating surface. Therefore, fewer active surface sites were available to VOC molecules. As a result, significantly less of the VOC mass was adsorbed, particularly for a long sampling time. However, within a very short sampling time, i.e., 1 min, no significant difference was observed at 47% RH compared to 0% RH. For the 47% RH, the reduction of the VOC uptake ranged from 0.6 to 3.7% at 1-min sampling time, compared with 2.2–6.2% reduction for 1 h. The reduction of adsorbed mass was more significant for the RH of 75%. In this case, the reduction of the mass adsorbed ranged from 10.6 to 18.1% for 1 min and from 17.2 to 21.2% for 1-h sampling. This indicates that the active surface sites are not saturated within a very short extraction time and are still available to VOC molecules. Thus, a short sampling time (far before equilibrium) can minimize the effect of RH on adsorption of VOCs on PDMS/DVB coatings.

New Sampling Devices. Findings presented in this research were used for the design and construction of new SPME sampling devices with an external fan and an attachment to commercial sampling pumps to enhance the extraction rate and equalize the extraction conditions during field air sampling. The full description of these devices and their field validation with conventional methods is presented in the forthcoming publication.³⁰ Compared to static extractions, rapid extraction conducted using moving air yielded greater amount of analytes adsorbed per unit of time, subsequently increasing the sensitivity of solid SPME fibers.

Rapid Water Sampling. On the basis of the results presented in this research, it is conceivable to use the same approach to direct water sampling and analysis. The existence of a boundary layer and its dependence on the water velocity and water viscosity is well documented in fluid mechanics literature. Thus, it will be possible to develop a similar methodology for diffusion-controlled extractions of VOCs in water. The liquid-phase mass-transfer

coefficients (D_l) for most VOCs are typically 3–4 orders of magnitude lower than the gas-phase mass-transfer coefficients (D_g). However, slower diffusion in water, can be partially offset by reduction of the boundary layer thickness for water under identical bulk fluid velocity. Thus, fast and diffusion-controlled extractions should be possible for water, with all benefits of short sampling time, such as the minimization of competitive adsorption effects.

CONCLUSIONS

Rapid air sampling methodology using absorptive SPME coatings and controlled air convection conditions was developed. A theoretical model for rapid extraction was formulated based on the diffusion through the interface surrounding the fiber. The presented model enables one to calibrate extracted analyte mass as a function of the gas-phase molecular diffusion coefficient, the analyte concentration, the sampling time, the air velocity, the air temperature, and the fiber geometry. This model compared well with experimental data obtained using very short sampling times and solid SPME coatings during controlled experiments with standard airborne VOCs. The use of short sampling times minimized the effects of competitive adsorption. The use of forced air increased the sensitivity of solid SPME coatings. An increased extraction temperature for rapid air sampling can be used to enhance the amount of analyte adsorbed per time, particularly for chemicals with high molecular weight and affinity for the coating.

For practical rapid sampling with solid SPME fibers, the appropriate sampling time for which the mass uptake is still linear should be first estimated. This can be accomplished by analyzing several samples that were collected with increasing sampling time and observing the mass uptake. It can be assumed that the capacity for the PDMS/DVB coating is approximately 30–40 ng for the analytes in this study. The appropriate sampling time can be optimized for existing conditions based on the rapid sampling model. Shorter sampling time should be used, when sampling for very volatile analyte, for high concentrations, and at high air velocity.

Considering the effectiveness of solid SPME coating in extracting significant amounts of analytes at very short sampling times, it can be concluded that this method is the fastest extraction-based technique for air sampling at typical airborne VOC concentrations. In combination with rapid chromatography, this approach can result in completion of the whole analytical process in less than 1 min.¹ None of the existing methods, besides the real-time methods, can provide quantitative data in such a short time. The method does not need calibrated externally since diffusion coefficients can be calculated for each analyte. In addition, quantification without identification is also possible since the gas diffusion coefficients for given unknown analyte can be estimated from the width of its chromatographic band. Findings presented in this study extend the existing fundamental knowledge related to air sampling and pave the way for new air sampling devices and novel applications for fast water sampling and analysis based on the diffusion-controlled extraction. The methodology presented in this research can be used to calibrate initial stages of extraction in other systems, e.g., liquid (PDMS or solvent) microextraction for analytes with high partition coefficients, in-tube SPME, and membrane extraction. As eq 4 indicates, the

increase of surface area of the contact between the sample matrix and the extraction phase would result in increase of the sensitivity of the extraction method. This fact can be explored when designing new sampling devices.

ACKNOWLEDGMENT

The authors thank the Center for Indoor Air Research (USA), the Center for Research in Earth & Space Technology, and SRI

Instruments for funding this study. Special thanks should go to Ben Smith for his help with editing the manuscript, and Stephen C. Weber for helpful discussions.

Received for review May 5, 2000. Accepted August 3, 2000.

AC000518L