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Calibration of Solid Phase Microextraction for Air Analyses Based on Physical Chemical Properties of the Coating

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Solid phase microextraction (SPME) with poly(dimethylsiloxane) (PDMS) is used to sample dynamic hydrocarbon standard gas mixtures with calibration for temperature, relative humidity, gas velocities, and gas concentrations. Equilibration times were found to vary from 15 to 450 s depending on the compound. Relative humidity greater than 90% at various temperatures was found to decrease analyte mass loading by 10%. Investigation of linearity with PDMS showed all of the analytes had a linear relationship between mass loaded at equilibrium and the gas concentrations studied. Analyte detection limits are better than those for conventional grab sampling (concentration with adsorbent tubes and analysis by gas chromatography and flame ionization detection). Partition coefficients (*K*) were established at various temperatures, yielding a linear relationship between log *K* and T^{-1}. The linear expression has a slope that is a function of the gas constant and the analyte heat of vaporization (ΔH^{v}) and a *y*-intercept that is a combination of terms among which include the gas constant, analyte ΔH^{v}, and activity coefficient; therefore, *K* values can be estimated using literature ΔH^{v} and ascertained at temperatures for which a *K* was not determined. This removes the restriction that calibration and air sampling must be carried out at the same temperature. A comparison of PDMS (100 μm) fiber lengths ($n = 13$) revealed an average fiber length of 1.02 ± 0.03 cm. An interfiber estimation of method precision ($n = 10$) yielded less than 9% RSD for all the test analytes. When a correction for fiber lengths was applied, the differences between the means of area counts for the individual fibers was statistically insignificant. SPME was successfully field tested as a grab sampler and an integrated sampler to analyze air at an industrial site, with excellent agreement to traditional air sampling methods. This work suggests that ambient and industrial air sampling with SPME is possible with essentially no calibration of the sampling device. It is only necessary to know the analyte's *K* to the fiber at various temperatures which is based on defined and empirically determinable physical constants.

Air can be sampled with a number of techniques, depending on the analyte of interest. Some of these techniques include grab sampling air with stainless steel canisters or nylon bags, concentration over a sorbent bed, colorimetric tubes, portable real-time detectors, passive monitors, and others.[1,2] The ideal scenario is invariably an extremely cost effective yet very accurate evaluation of the airborne analyte concentration, which are two opposing demands. In practice, an acceptable balance is always sought among the speed of analysis, accuracy, practicality of sampling, the instrument used for quantitation, and total cost. The sampling and analysis techniques of choice depend on both the analyte of interest and the ultimate use of the results. For example, nylon bags are quite useful for tracer gas studies involving sulfur hexafluoride[3] but would not be practical to study airborne polyaromatic hydrocarbons due to losses of those hydrocarbons on the walls of the bags. Traditional methods to examine airborne concentrations of aliphatic and aromatic compounds include active air sampling[2] and whole air sampling.[4] Active air sampling is facilitated with mass flow-controlled pumps drawing the air suspected to contain the analyte(s) of interest over a bed of charcoal or other sorbents with subsequent thermal or chemical desorption followed by separation with GC and detection with flame ionization detectors (GC/FID) or other types of detectors. These sampling techniques are quite useful but at the same time are cumbersome, bulky to ship to field studies, can be difficult to employ at a moment's notice, and require toxic eluants for chemical desorption or costly thermal sorbent desorbers. Whole air sampling in stainless steel canisters alleviates some of the drawbacks with active sampling yet they introduce different problems such as the requirement for costly GC interfaces. Passive sampling for airborne hydrocarbons with charcoal beds[2,5] provides a good substitute to the active sampling methods, but the analysis maintains the use of toxic solvents for chemical desorption and the system is limited by interfering organics from the charcoal bed holder, which increase method detection limits.

Solid phase microextraction (SPME) is a relatively new technique which is shown in this paper to be a viable alternative to sampling airborne compounds just as it has shown to be a viable alternative to extracting a multitude of target analytes from a myriad of aqueous systems and/or their corresponding headspace.[6−10,15] Sampling air with SPME provides a significant advantage over traditional methods, both active sampling and

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whole air sampling, and it is potentially useful in a number of scientific applications ranging from environmental engineering studies to industrial hygiene monitoring and indoor air quality surveys. It can also be used in scientific applications where fast, accurate, reproducible, cost effective, simple to deploy, and reusable sampling devices are required. SPME uses no solvents or solutes except for calibration of the analytical instrument, and it provides the analyst with an extremely sensitive tool for sampling and analysis.[6,7]

Preliminary work using SPME to sample airborne volatile organic hydrocarbons (VOCs) has been reported.[11] This work focused predominantly on controlled static sampling conditions in gas sampling bulbs and stainless steel canisters. Under static sampling conditions, the analytes absorb onto the poly(dimethylsiloxane) (PDMS) and eventually reach equilibrium. The time to reach equilibrium depends on the kinetics of the overall process of analyte uptake by the fiber, which is based in part on the rate of analyte diffusion in the air and the distribution coefficient of the analyte between the air and PDMS.[6,7] Strong agitation of the analyte mixture and matrix has been shown to be the ideal technique to study analyte concentrations in aqueous systems for both direct extraction and extraction from headspace,[9] and so one can deduce this is also true for air sampling. The ideal air system for testing SPME is one where the air is dynamic, i.e., a constant flow rate of a gas mixture containing a unchanging concentration of the analytes of interest which passes over the SPME sampling device. In contrast to static sampling, this system virtually eliminates the wall effects of the sampling vessel and presents a continual concentration of analytes to the SPME.

This paper discusses the use of SPME to sample standard gas mixtures of airborne hydrocarbons under a number of different conditions including different temperatures, relative humidities, gas velocities, and analyte concentrations. Also, intra- and interfiber comparisons of reproducibility and accuracy, respectively, are studied to demonstrate that each fiber yields statistically similar results of sampling and analysis because each separate fiber is ostensibly a separate sampling and analysis device. The paper shows how simple it is to sample air with SPME knowing both the temperature and relative humidity (RH). In addition, data are presented showing results obtained from an air sampling session that occurred in an industrial environment for grab sampling and a preliminary study on the use of SPME as an integrated sampling device.

THEORY

In air, the K at a fixed temperature for an analyte between the PDMS fiber and air can be described by the Nernst distribution law, modified and shown in eq 1[12] (where the units for C_{fiber} and

$$K = C_{\text{fiber}}/C_{\text{air}} \tag{1}$$

C_{air} can be μg/L or mg/m^3). Equation 1 can be rearranged to eq 2 to provide an expression to determine unknown airborne

$$C_{(\text{air})} = C_{(\text{fiber})}/K \quad (\text{at a fixed } T) \tag{2}$$

concentrations of analytes provided the sampling and K are determined at the same temperature and provided there are no interfering processes competing with the analyte uptake such as with high relative humidities.[11] An understanding of the dependence of K on temperature is required in order to provide a theoretical expression for eq 2 that can be used to determine the K at any temperature. This requires a closer examination of K as it relates to the distribution of an airborne analyte between the fiber and air. For the dynamic process of analyte uptake on the fiber it must first be assumed that the C_{fiber} does not change with time; i.e., the system is at steady state where $dC_f/dt = 0$. We can describe the mass uptake of the analyte on the fiber in the system by the analyte's partial pressure using Raoult's law for a nonideal solution as shown in eq 3, where p is the partial

$$p = \gamma'_i x_i p^\circ \tag{3}$$

pressure of the analyte, p° is the pure analyte vapor pressure, x_i is the mole fraction of the analyte in the fiber, and γ'_i is the analyte activity coefficient in the fiber. It is more convenient to describe the analyte concentration instead of mole fraction and so eq 4a shows the constant A, which is used to convert the mole

$$\gamma'_i x_i = \gamma'_i A C_{\text{fiber}} \tag{4a}$$

$$\gamma'_i A C_{\text{fiber}} = \gamma_i C_{\text{fiber}} \tag{4b}$$

$$A = x_i/C_{\text{fiber}} \tag{4c}$$

fraction to concentration, and eq 4b shows a new activity coefficient, which includes the constant A which is defined in eq 4c, where γ_i is the new activity coefficient containing A. Substituting eq 4b into eq 3 we get

$$p = \gamma_i C_{\text{fiber}} p^\circ \tag{5}$$

Equation 5 can be combined with the ideal gas law yielding

$$C_{\text{air}} RT = \gamma_i C_{\text{fiber}} p^\circ \tag{6}$$

Equation 6 can be rearranged and combined with the Clausius−Clapeyron eq for p° followed by taking the logarithm yielding

$$\log K = \frac{\Delta H^{\text{v}}}{2.303RT} + \left[\log\left(\frac{RT}{\gamma_i p^*}\right) - \frac{\Delta H^{\text{v}}}{2.303RT^*}\right] \tag{7}$$

where p^* is the analyte vapor pressure at a known temperature T^* for a pure solute, ΔH^{v} is the heat of vaporization of the pure solute, and T is the temperature of interest. We can see from eq 7 there is a linear relationship between log K and T^{-1} as in the common expression $y = mX + b$. From this we can simplify eq 7 into

$$\log K = a\left(\frac{1}{T}\right) + b \tag{8}$$

where

$$a = \frac{\Delta H^{\text{v}}}{2.303R}, \quad b = \left[\log\left(\frac{RT}{\gamma_i p^*}\right) - \frac{\Delta H^{\text{v}}}{2.303RT^*}\right], \quad X = \frac{1}{T}$$

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From eq 8, we see the *y*-intercept has a small dependence on temperature, but careful examination reveals the dependence is significantly smaller than that for the slope; therefore, there is little error associated in ignoring the dependence of the *y*-intercept on temperature. Equation 8 can be rearranged and combined with eq 2 yielding

$$C_{\text{air}} = (\text{mg on fiber})10^{-((a/T)+b)}V_f^{-1} \qquad (9)$$

where C_{air} is in mg/m^3, the V_f is the fiber volume expressed in m^3 ($\sim 690 \times 10^{-12}$ m^3 for the 100 μm thick fiber and $\sim 140 \times 10^{-12}$ m^3 for the 30 μm thick fiber), and T is in K. Equation 9 provides a means to determine the concentration of an analyte in air given constants a and b are known as well as the sampling temperature. Careful attention should be made to the fiber lengths since it is possible to overestimate or underestimate the actual fiber volume based on the assumption the fiber length is 1.00 cm, as will be shown in Results and Discussion.

It is convenient to express the concentration of an airborne analyte in parts per million volume by volume (ppm_v) in air since it includes the molar volume and sample temperature.

$$\text{ppm}_{v(\text{air})} = (\text{mg on fiber})\frac{R}{\text{MW}PV_f}\left[\frac{T}{10^{((a/T)+b)}}\right] \qquad (10)$$

The symbol α can be used for $R/\text{MW}PV_f$, yielding a constant for a given analyte and having no dependence on temperature; the result is shown in

$$\text{ppm}_{v(\text{air})} = (\text{mg on fiber})\alpha[T/10^{((a/T)+b)}] \qquad (11)$$

It is possible to provide data relating the temperature and a and b values for a specific analyte with the expression $[T/10^{((a/T)+b)}]$ and define this as β. Equation 12 shows the new expression,

$$\text{ppm}_{v(\text{air})} = (\text{mg on fiber})\alpha\beta \qquad (12)$$

which can be used to determine the airborne concentration of an analyte at any temperature. Equation 12 simply requires the analyst to determine the mass of analyte loaded on the 100 or 30 μm PDMS fiber and then look up the appropriate α and β values for the analyte of interest with a specific fiber at a specific temperature. It is also possible to replace β with $[T/K]$ in eq 12 when the analyte's K was determined at the sampling temperature. A margin of potentially tolerable error is introduced if one ignores the temperature dependence of K for a narrow temperature range such as 296−300 K and uses the K determined at 298 K for quantitative analysis; this is not recommended but can be used to provide a reasonable K to estimate concentration.

EXPERIMENTAL SECTION

Chemicals. Benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, 1,3,5-trimethylbenzene (mesitylene), α-pinene, *d*-limonene, *n*-pentane, *n*-hexane, and *n*-undecane were purchased from Sigma-Aldrich (Mississauga, ON). Carbon disulfide was purchased from BDH (Toronto, ON). All chemicals were used as purchased.

Materials. Nitrogen, helium, and hydrogen gases for flame ionization detection and compressed air for standard gas generation as well as a two-stage regulator for the compressed air were purchased from Praxair (Waterloo, ON, Canada). Air for the flame ionization detector was generated from an air generator purchased from Balston. Very fine metering valves, $^1/_8$ and $^1/_{16}$ in., and adapters and tees for $^1/_8$ in. tubing were purchased from Swagelock (Ontario). The syringe pump used to deliver the analyte mix for standard gas generation was purchased from Sage Syringe Instruments.

All SPME with PDMS 100 and 30 μm fiber assemblies and holders were purchased from Supelco (Supelco, Canada) as well as all syringes, impinger, charcoal scrubber, air diffusers, silica gel, bubble flow meters, columns, passive badges, charcoal tubes, and vials.

Preparation of Analyte Mixture. A standard mixture of benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, mesitylene, α-pinene, *d*-limonene, *n*-pentane, *n*-hexane, and *n*-undecane was prepared by adding 0.75 g of each analyte, starting with *n*-undecane, into a Teflon-capped flask. The mixture was then thoroughly mixed and transferred to each of six 1.8 mL Teflon-capped vials, leaving no headspace. This mixture, which was made up of 9.1% (w/w) of each analyte, was used in the syringe pump delivery system for generating the standard gas.

Standard Gas-Generating Device. A standard gas-generating device was constructed as shown in Figure 1. All copper and stainless steel tubing connecting the compressed air to the standard gas-generating device was thoroughly cleaned with solvent, allow to dry, and then flamed. All air was scrubbed over a bed of a charcoal. Air flow rates into the mixing chamber were controlled with a very fine metering valve maintained at 20 psi head pressure. The 20 L chamber was lined with two consecutive layers of $^1/_{16}$ in. Teflon, including the inside base, and covered with a $^1/_8$ in. thick piece of Teflon which was covered with $^1/_4$ in. thick aluminum plate and bolted to an aluminum base, thus squeezing the top layer of Teflon to the lip of the container. Pressure tests with helium in the chamber at 10 psi and a leak detector proved the chamber was air-tight. The outside of the chamber was uniformly covered in a coil of $^3/_8$ in. copper tubing through which water was flowing from a temperature-controllable water bath, thus providing a constant temperature to the chamber. All chamber temperatures were measured inside the chamber. The chamber was allowed to reach steady state after a minimum of 10 volume changes (aerodynamic residence times), after each temperature change or alteration in gas concentration. The mixing port and air line to the chamber were heated to 323 K with heat tape and a variable voltage controller. For humidification, the air was diverted through two consecutive water-immersed diffusers inside sealed containers at ambient temperature. Relative humidity in the chamber was determined by drawing air at a known flow rate directly from inside the chamber to a preweighed impinger containing dry indicating silica gel. The airborne water concentration was then calculated and expressed in moles per lit. The corresponding pressure of that concentration of water at 1 atm was calculated using the ideal gas law, and this pressure was then taken as a percentage of the equilibrium vapor pressure of water at that temperature[14] resulting in percent relative humidity.

A 500 μL Hamilton gas-tight syringe was used in the syringe pump to deliver the analyte mixture. The syringe pump was

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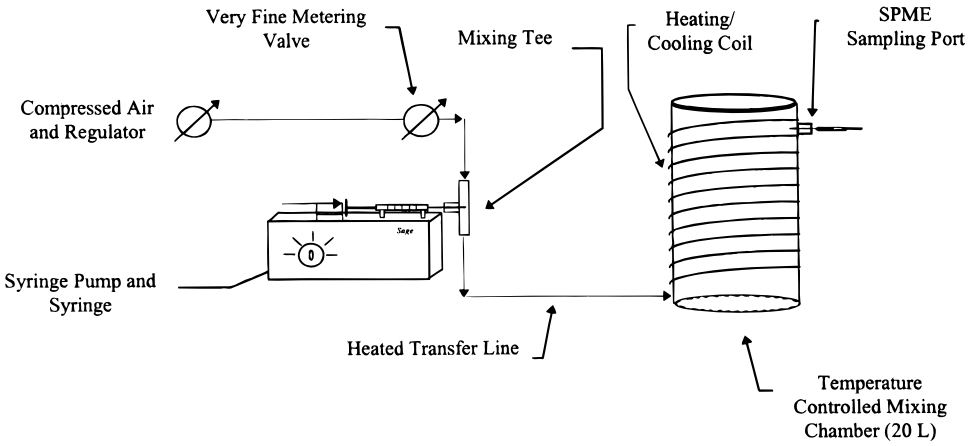

Figure 1. Schematic representation of the standard gas-generating device. Humidification system not shown.

calibrated for analyte delivery of the analyte mixture to 4.4 mg/h into the mixing tee. With an air flow rate of 200mL/min, the expected total hydrocarbon gas concentration was 0.37 mg/L at normal temperature and pressure (NTP) and ~34 μg/L at NTP for an individual analyte. The individual analyte concentration at NTP was confirmed using a standard air sampling technique described below.

Validation of Standard Gas Mixture Analyte Concentrations. Hydrocarbons in air concentrations from the standard gas-generating device at NTP were verified following National Institute for Occupational Safety and Health (NIOSH) methods 1500 and 1501 for the determination of airborne hydrocarbons. A mass flow-controlled air sampling pump equipped with a very fine metering valve was used to draw air through small charcoal tubes at 50 mL/min which was calibrated with a bubble flowmeter. Chemical desorption from charcoal was facilitated with 1.0 mL of CS_2 in Teflon-capped 4 mL vials. All air sample measurements were carried out in quadruplicate and repeated after a period of days in quadruplicate for confirmation.

SPME with PDMS Sampling of Standard Gas Mixtures. The technical aspects on the SPME sampling device and its use have been thoroughly described.[6,7] Unless otherwise specified, all SPME sampling took place inside the chamber at 298 K. Each fiber was injected at least five times for repeatability studies, new chamber temperatures, or relative humidities whereas at least nine samples were acquired for each new air concentration.

A standard gas concentration of 34 μg/L at 298 K was chosen for both intrafiber reproducibility and interfiber comparisons. Ten repeats were carried out for intrafiber reproducibility. The interfiber comparison was carried out with three different fibers selected from three different lots spanning months of production. Two of the three fibers were analyzed five times and the third was analyzed six times. Each fiber was consecutively used to sample the standard gas mixture. The study of fiber geometry was carried out on 13 different fibers from a number of production lots spanning months of production.

Run-to-run carryover for one fiber was established by exposing the fiber for a given time to the standard gas and then desorbing the analytes in the injector port as described. The fiber was then retracted while still in the injector and then exposed for another run. Other fiber blanks included leaving the fiber retracted while covered with a new and clean silicone septum.

Appropriate fiber desorption times were established by desorbing the fibers for less than 1 min at the injector temperature, then withdrawing the fiber from the injector and placing a silicone septum over the end, and then injecting the fiber again. A 2 min desorption time proved to be sufficient for more than 99% removal of analytes from the fiber with an injector temperature of 225 °C.

Linearity and Detection Limits with PDMS. The standard gas mixture concentration was increased and decreased in the chamber by decreasing the flow rate and increasing the air flow rate into the mixing tee, respectively. The concentration range studied was from 0.60 to 1333 ng/L. Detection limits were established by analyzing eight repeats of blank fiber injections and multiplying by three the noise for the respective retention times.

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

The instrument was checked daily for calibration using a liquid midpoint calibration standard, and any deviations in area counts greater than 15% required reinjection of that standard; if still greater then 15%, the instrument was recalibrated with a five point calibration. In addition, quality of peak shapes, resolution, and retention times were carefully monitored to ensure all chromatography was within specification.

Field Sampling with SPME Using PDMS. Four different methods were used to determine the airborne concentration of styrene from a styrene-based resin used in an industry. Charcoal tubes with active sampling, charcoal passive badge monitors, a portable photoionization detector (PID) based on active air sampling, and the SPME 100 μm PDMS were all used in this study. The active sampling through charcoal tubes was carried out with the same equipment as mentioned in the validation of standard gas; the sampling and analysis method was NIOSH method 1501 except that air was drawn through the charcoal tube

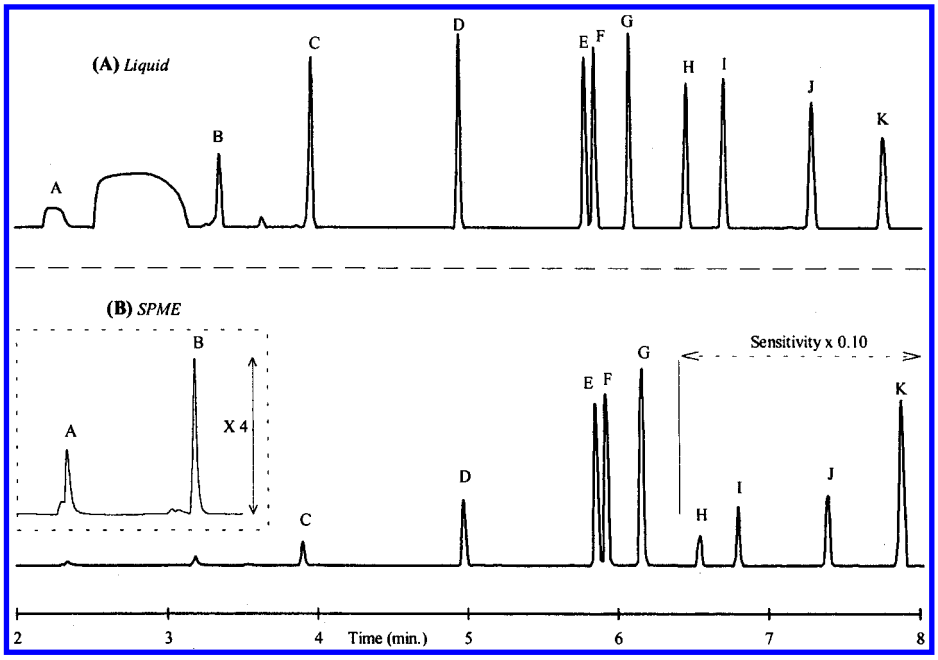

Figure 2. (A) Chromatograms of charcoal tube and (B) PDMS SPME extraction of the standard gas (34 μg/L, 298 K) from the standard gas-generating device. Peak identification: (A) *n*-pentane, (B) *n*-hexane, (C) benzene, (D) toluene, (E) ethylbenzene, (F) *p*-xylene, (G) *o*-xylene, (H) α-pinene, (I) 1,3,5-trimethylbenzene, (J) *d*-limonene, and (K) *n*-undecane.

at 100 mL/min. 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 isobutylene at 296 K and certified by the supplier of the equipment. The supplier indicated styrene response on the PID was 42% of that for isobutylene. It was possible to use a PID in this study because previous analyses at other similar locations and activities showed greater than 99% styrene in air. For SPME with PDMS, eight 100 μm PDMS fibers were each conditioned at 250 °C for 1 h and 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 integrated sampling, the fibers were left retracted in the assembly and exposed to the air for 30 min concurrent to the acquisition of 30 min active sampling through charcoal tubes. Immediately after sampling with SPME with PDMS, all of the fibers were removed from the fiber holder and retracted ~1.5 cm into the barrel of its assembly, which was followed by capping the end with a new and clean 6 mm silicone septum, and placed 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.

RESULTS AND DISCUSSION

Validation of Standard Gas Generation Device. Figure 2A shows the typical chromatograms obtained for the charcoal tube samples of the standard gas mixture containing the 11 analytes under study. These data were used to validate the concentration of the individual analytes in the gas mixture. For the purpose of presenting a comparison, the corresponding SPME with PDMS extraction of the same gas mixture is shown in Figure 2B. Peak assignments were confirmed with gas chromatography/mass spectrometry (mass spectra not shown). Table 1A summarizes the validation data using the peak areas for analytes from the charcoal tube air samples for the standard gas-generating device at 298 K for a theoretical analyte concentration of 34 μg/L at NTP. The data indicate there is excellent agreement between the actual standard gas concentrations and the expected analyte concentrations at 298 K. Equation 13 was used to provide a flexible

$$C_{\mathrm{air}_{(\mathrm{any\ T,K})}} = C_{\mathrm{air}_{(298\ \mathrm{K})}}(T^*/T_X) \qquad (13)$$

relationship between temperature and the C_{air} from the standard gas-generating device (Appendix). T^* is 298 K in this case and T_X is the temperature at which knowledge of the new C_{air} is required. This expression is used to estimate the gas concentration for a given temperature range provided the gas concentration is established at a known temperature T^*. From eq 13, a standard gas concentration of 34 μg/L at 298 K is reduced by ~4% at 311 K and increased by ~3% at 290 K. These concentration differences are important in order calibrate the standard gas-generating device at different temperatures specifically for the relationship between K values as a function of temperature (see below).

Absorption/Time Profiles for PDMS at Standard Gas Concentrations. Absorption/time profile studies were carried out to determine equilibration times for each analyte at 34 μg/L at NTP with the 100 μm PDMS. Figure 3 shows representative absorption/time profiles for a few of the test analytes and Table 1B summarizes the equilibration times for each analyte. In comparison to previous work with similar compounds, these results indicate that equilibration times are smaller for dynamic sampling compared to static sampling.[9,11] This is logical because in both static and dynamic sampling the time to reach equilibrium is limited by the analyte rate of diffusion in both the gas and fiber phases, but that in a static sampling system the former rate is more significant in comparison to dynamic sampling; in dynamic

Table 1[a]

	A	B	C		D		E	
analyte	% Er	Eq (s)	*K* (30 μm PDMS)	*K* (100 μm PDMS)	% RSD day 1	% RSD day 2	LOD, μg/L	r^2
n-pentane	5	15	100	95	6.1	8.5	5.5	0.99999
n-hexane	1	45	170	150	4.7	2.8	2.6	0.99999
benzene	1	60	260	300	2.0	2.2	1.2	0.99999
toluene	0	60	710	880	5.1	2.3	0.41	0.99999
ethylbenzene	1	60	2000	2100	2.0	2.2	0.16	0.99999
p-xylene	1	90	2300	2400	2.1	2.4	0.15	0.99997
o-xylene	−3	120	3100	3100	2.7	2.5	0.12	0.99997
α-pinene	0	160	4300	4500	2.4	2.2	0.09	0.99999
mesitylene	0	150	5900	5800	2.2	2.4	0.06	0.99998
d-limonene	1	300	10300	10300	2.4	2.7	0.04	0.99999
n-undecane	0	450	25000	25000	2.7	3.5	0.02	0.99999

[a] Key: (A) Validation data for chamber with percent relative error (%Er). (B) Summary of equilibration times for 100 μm PDMS SPME. (C) Summary of *K* for 100 and 30 μm PDMS SPME using standard gas (34 μg/L, 298 K). (D) Summary of PDMS intrafiber reproducibility for n = 10 repeats (34 μg/L, 298 K). (E) Detection limits and r^2 for 100 μm PDMS SPME for various standard gas concentrations at 298 K. The LOD is based on three times the noise for that peak for n = 8 repeats of fiber blank injections.

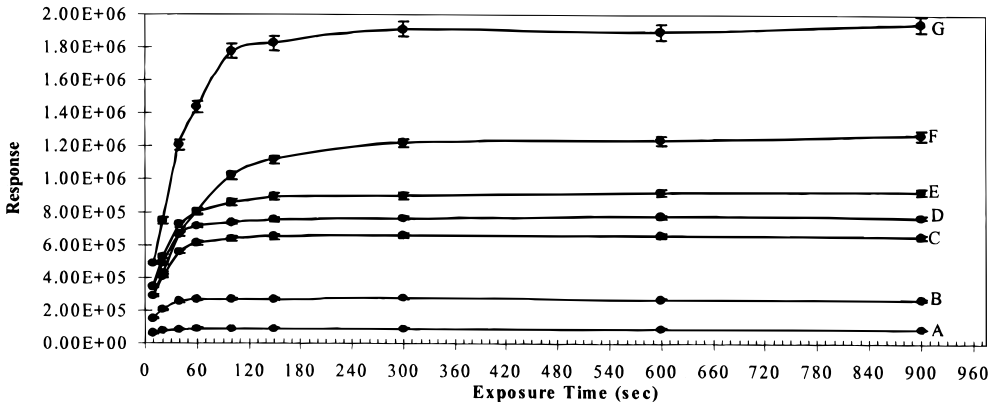

Figure 3. Representative absorption/time profiles using PDMS SPME extraction of standard gas (34 μg/L, 298 K) for (A) benzene, (B) toluene, (C) ethylbenzene, (D) *p*-xylene, (E) *o*-xylene (F) α-pinene, and (G) 1,3,5-trimethylbenzene. The lines connecting the points in no way represent a mathematical relationship.

sampling, a fresh source of analyte is constantly delivered to the fiber per unit of time, thus minimizing the dependence on analyte diffusion in air. Only those analytes with small diffusion coefficients are subject to longer equilibration times as evidenced by the equilibration time for *n*-undecane, while compounds such as *n*-hexane have short equilibration times.

Determination of Analyte Air/PDMS *K* Values Using the Standard Gas-Generating Device. Table 1C summarizes the *K* obtained for each analyte using both the 100 and 30 μm PDMS fibers with a 10 min equilibration time and the conditions described in the previous section. The *K* provides a measure for the distribution of an analyte from air to PDMS as shown with eq 2 and so can be used to estimate analyte detection limits in air because detection limits increase as *K* decreases for a fixed mass of absorbed analyte (eq 12). These *K* values are vital to the determination of unknown concentrations of target analytes in air in that quantitation would not otherwise be possible without extensive external calibration.

***K* as a Function of Temperature.** Figure 4 demonstrates representative curves for the linear relationship between log *K* for each analyte and PDMS and the inverse of temperature. Table 2 summarizes the slope (*a*) and *y*-intercept (*b*) values (see eq 8, theory) and the r^2 for the curves for each of the studied analytes. In addition, Table 2 shows the calculated a^L values based on literature ΔH^v data[14] for each of the 11 analytes studied and compares the observed *a* values. The data indicate there is very good agreement between the calculated a^L values using literature ΔH^v and the observed *a* values determined using eq 8. This indicates it is possible to use literature ΔH^v values to determine *a* values. The *b* values can be determined with eq 8 by acquiring *K* for the target analyte at a specific temperature and calculating *a* with the literature ΔH^v. Also shown in Table 2 are the α and β (298 K) values for each analyte, which can be used to determine the airborne analyte concentration as per eq 12.

In order to substantiate the argument eq 8 can be used to predict *K* values at different temperatures, *K* values were determined for each of the 11 analytes at 296 K, a temperature that was not used to establish the relationship between *K* and temperature, and the data compared to the estimated *K* value using eq 8 with the data summarized in Table 3. The data indicate there is good agreement between the estimated *K* and actual *K*, which in part supports the validity of eq 8 for the studied temperature range. Given the studied temperature range encompasses almost all ambient air sampling temperature conditions, it is unlikely significantly higher or lower temperatures are required to complete the understanding of dependence of *K* on temperature for PDMS.

Comparison between Different Face Velocities on SPME Uptake of Airborne Analytes. The question as to whether there is a difference between static and dynamic sampling and between

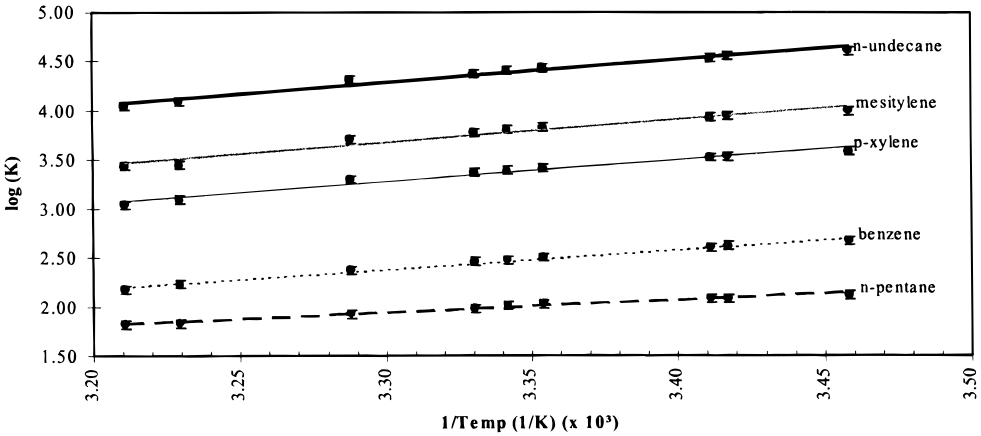

Figure 4. Representative plots for pentane, benzene, *p*-xylene, mesitylene, and *n*-undecane demonstrating the linear relationship between log *K* and the inverse of temperature.

Table 2. Summary of α and *β* and *a* and *b* Values for Each Analyte from the Slope and *y*-Intercept of log *K* as a Function of Inverse Temperature[a]

analyte	α	*β*, 298 K	*a* (exp)	*b*	r^2	$a^{L\ (lit)}$	% diff *a* and a^L
n-pentane	1.65×10^6	3.14	1278	−2.280	0.99	1441	−13
n-hexane	1.38×10^6	1.99	1944	−4.324	0.98	1667	14
benzene	1.52×10^6	0.994	2025	−4.304	0.99	2241	−11
toluene	1.29×10^6	0.304	2189	−4.419	0.98	2047	6
ethylbenzene	1.12×10^6	0.142	2252	−4.208	0.98	2032	10
p-xylene	1.12×10^6	0.124	2234	−4.097	0.97	2144	4
o-xylene	1.12×10^6	0.0962	2316	−4.283	0.97	2185	6
α-pinene	1.12×10^6	0.0663	2301	−4.071	0.95	2144	7
mesitylene	9.89×10^5	0.0514	2364	−4.127	0.96	2298	3
d-limonene	9.89×10^5	0.0289	2454	−4.199	0.96	2296	6
n-undecane	7.61×10^5	0.0119	2292	−3.278	0.97	2509	−9

[a] See theory for a description of α, *β*, *a*, and *b* values. Also shown are the calculated a^L values using literature ΔH^{v} [14] and the expression for *a* and *b* in eq 8.

Table 3. Comparison of *K* Values Estimated with Eq 8 and Compared to the Actual *K* Values Determined at 296 K

analyte	est *K*	*K* at 296 K	% Er
n-pentane	110	105	5.7
n-hexane	178	174	2.2
benzene	351	345	1.9
toluene	968	967	0.1
ethylbenzene	2572	2468	4.2
p-xylene	2886	2731	5.7
o-xylene	3554	3388	4.9
α-pinene	5151	5500	−6.5
mesitylene	7409	7282	1.7
d-limonene	12578	12362	1.7
n-undecane	29793	29851	0.4

laminar gas flow and turbulent gas flow was addressed (Table 4A). The standard gas was sampled directly from inside the chamber where the air flow is laminar and compared to sampling at the mouth of the sampling port which had turbulent flow. Laminar (Re <2000; see below) and turbulent flow (Re >3000, see below) were calculated using the expression for Reynolds number (Re) as in the eq $\mathrm{Re} = 2Rd\vartheta/\eta$, where *R* is the radius of the sampling port, *d* is the density of the gas, ϑ is the bulk velocity of the gas, and η is the coefficient of viscosity.[16] In addition, static sampling the same standard gas concentration provided an estimate of whether gas velocity has an effect on sampling (Table 4A). The data indicate there is essentially no difference between laminar and turbulent flow. Also, there is no significant difference (in analyte mass loading) between a 10 min exposure time for both static and dynamic sampling with a standard gas at NTP for analytes with *K* less than 5000, but there is a difference for analytes with *K* values greater than 6000. This is explained by considering the phenomenon that for an increasing homologous series of hydrocarbons one finds an associated decrease in the analyte's rate of diffusion,[18] thus indicating an increased time is required for the analyte to reach equilibrium between the air in the bulk of the sample and PDMS. This was confirmed by doubling the PDMS exposure time in the static sampling bulb and comparing the observed area counts to those from PDMS exposure to the dynamically generated standard gas. The data indicate that under these conditions there is no statistically significant difference (95% confidence level) between static and dynamic sampling, only that an increased exposure time is required to reach equilibrium under static conditions compared to the same steady-state levels from dynamic conditions for those compounds with *K* larger than 6000.

Intrafiber Reproducibility and Interfiber Comparison. An intrafiber reproducibility study ($n = 8$) for one fiber and an interfiber comparison study (for 10 different fibers) was carried out with a standard gas concentration of 34 μg/L at 298 K. The results from the intrafiber reproducibility are summarized in Table 1D. The data indicate there is excellent day-to-day consistency in the intrafiber reproducibility. An interfiber estimation of method precision for the 10 different fibers yielded from approximately 3−9% RSD (Table 5) for each of the 11 analytes studied. In order to use the commercially available SPME 100

Table 4. (A) Comparisons between Static and Dynamic Sampling and Turbulent and Laminar Flow ($n = 4$) and (B) Effect of Humidity (% RH) on the Analyte Mass Loaded on the 100 μm PDMS Fiber ($n = 4$)[a]

	(A) mean area counts (8.5 μg/L at 297 K)			(B) mean area counts (33 μg/L at 310 K)				
analyte	static (no flow)	laminar flow	turbulent flow	0	30	40	75	95
n-pentane	5.08×10^3	5.13×10^3	5.04×10^3	1.16×10^4	1.13×10^4	1.15×10^4	1.11×10^4	9.82×10^3
n-hexane	1.02×10^4	1.05×10^4	9.79×10^3	2.165×10^4	2.11×10^4	2.32×10^4	2.12×10^4	1.95×10^4
benzene	2.25×10^4	2.31×10^4	2.16×10^4	4.65×10^4	4.63×10^4	4.83×10^4	4.69×10^4	4.18×10^4
toluene	6.59×10^4	6.80×10^4	6.37×10^4	1.25×10^5	1.26×10^5	1.25×10^5	1.22×10^5	1.11×10^5
ethylbenzene	1.64×10^5	1.68×10^5	1.57×10^5	2.88×10^5	2.95×10^5	2.94×10^5	2.92×10^5	2.61×10^5
p-xylene	1.95×10^5	2.00×10^5	1.84×10^5	3.22×10^5	3.30×10^5	3.27×10^5	3.38×10^5	2.88×10^5
o-xylene	2.45×10^5	2.61×10^5	2.34×10^5	3.94×10^5	4.02×10^5	4.00×10^5	4.27×10^5	3.54×10^5
α-pinene	3.22×10^5	3.34×10^5	3.14×10^5	4.77×10^5	4.97×10^5	4.96×10^5	4.81×10^5	4.35×10^5
mesitylene	4.59×10^5	4.67×10^5	4.47×10^5	7.94×10^5	8.22×10^5	8.26×10^5	7.93×10^5	7.16×10^5
d-limonene	7.67×10^5	7.79×10^5	7.45×10^5	1.22×10^6	1.27×10^6	1.27×10^6	1.23×10^6	1.10×10^6
n-undecane	1.88×10^6	1.88×10^6	1.82×10^6	3.16×10^6	3.25×10^6	3.25×10^6	3.11×10^6	2.76×10^6

[a] The high temperature was chosen to challenge the fiber at high absolute humidity.

Table 5. Summary of Responses for an Interfiber Comparison (10 Different Fibers)[a]

analyte	average	std dev	% RSD
n-pentane	1.91×10^4	1.66×10^3	8.7
n-hexane	4.49×10^4	3.86×10^3	8.6
benzene	9.66×10^4	3.49×10^3	3.6
toluene	2.74×10^5	1.40×10^4	5.1
ethylbenzene	6.68×10^5	2.09×10^4	3.1
p-xylene	7.34×10^5	2.61×10^4	3.6
o-xylene	9.78×10^5	5.13×10^4	5.2
α-pinene	1.35×10^6	4.82×10^4	3.6
mesitylene	1.92×10^6	7.46×10^4	3.9
d-limonene	3.22×10^6	1.15×10^5	3.6
n-undecane	7.54×10^6	2.45×10^5	3.3

[a] At 34 μg/L (298 K, 10 min equilibration time, 100 μm PDMS).

or 30 μm PDMS for general air sampling, one must demonstrate that each similarly constructed fiber from any lot number can indeed yield the same concentration of analyte in air especially since the range in precision is so narrow. The *t*-test was used to compare the method accuracy of three different fibers (from three different lots), assuming a normal distribution. The *t*-test is preceded by an *F*-test[19] which is required to compare the variances of those means for each analyte since unequal variances do not allow the use of the standard two-tailed *t*-test. Each of three fibers were arbitrarily labeled A, B, and C. The results from fiber A were compared to B and C and then fiber B was compared to fiber C. All variances passed the *F*-test at the 95% confidence level (data not shown). These three fibers were then used for the *t*-test study, Table 6. The results show there is a statistically significant difference between the fiber comparisons for some of the analytes, but this difference was attributed to different fiber lengths. Indeed, a detailed microscopic examination of 13 different fibers from a number of different lots demonstrated that fiber lengths ranged from 0.98 to 1.06 cm with an average length of 1.02 ± 0.30 cm. When a correction for fiber length was applied to fiber C, the differences between the individual fibers as estimated with the *t*-test were found statistically insignificant at the 95% confidence level (Table 6). These results strongly implicate the fiber originally failed the *t*-test comparisons for method accuracy due to inconsistent fiber lengths.

Linearity and Detection Limits with PDMS. Table 1E summarizes the data obtained from the study of r^2 and limits of detection for each analyte with PDMS using the standard gas-generating device at constant temperature. Figure 5 shows representative calibration curves for benzene, ethylbenzene, α-pinene, and *d*-limonene. The data indicate that, as expected, those compounds with larger *K* have lower limits of detection. This is because (see eq 2) the actual air concentration decreases as *K* increases for a fixed mass of analyte loaded on the fiber. Pentane's *K* is smaller than undecane's and consequently pentane has a higher detection limit than undecane under the same conditions of sampling and analysis. Examination of eq 12 indicates that lower detection limits are possible with decreasing β primarily due to the increase in *K* with decreasing temperature. In addition, it is possible to see from eq 10 that a smaller fiber coating volume such as that for the 30 μm thick PDMS fiber will increase the analyte detection limit compared to the larger fiber coating volume for the 100 μm thick fiber. This also indicates there is flexibility in air sampling should the analyte under study have an extremely large *K*, e.g., 100000, or if it is present at very large concentrations, e.g., greater than 1 mg/L; the 30 μm fiber can be used for anticipated high *K* analyte and/or analyte concentrations whereas the 100 μm fiber can be used for lower *K* analyte and/or analyte concentrations.

Detection limits by GC/FID for conventional sampling and analysis methods for most of these analytes are reported to be from 1 to 10 μg/sample, depending on the volume of air sampled whereas SPME with 100 μm PDMS has a conservative detection limit of 0.3 ng/sample with the same instrumental conditions. The higher detection limits for the former are due predominantly to the chemical background of the adsorbent, are lower with a higher quality of charcoal and chemical eluant, and are not better for passive sampling with charcoal.[20] In addition, further examination of the detection limits with active or passive sampling with charcoal tubes indicates the detection limits increase significantly when these devices are used for grab sampling. For example, a

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Table 6. *t*-Test Comparison at the 95% Confidence Level ($t_{crit} = 2.447$) ($n = 4$ for each fiber)[a]

A

	fiber A		fiber B		fiber C	
	mean	std dev	mean	std dev	mean	std dev
n-pentane	1.207×10^4	1.86×10^3	9.804×10^3	1.340×10^3	1.010×10^4	1.102×10^3
n-hexane	2.283×10^4	1.65×10^3	2.044×10^4	1.456×10^3	2.038×10^4	2.102×10^3
benzene	4.886×10^4	3.01×10^3	4.478×10^4	1.948×10^3	4.349×10^4	1.908×10^3
toluene	1.415×10^5	8.84×10^3	1.329×10^5	2.595×10^3	1.255×10^5	3.390×10^3
ethylbenzene	3.482×10^5	2.05×10^4	3.206×10^5	1.432×10^4	3.113×10^5	1.038×10^4
p-xylene	3.846×10^5	2.40×10^4	3.545×10^5	1.596×10^4	3.411×10^5	8.615×10^3
o-xylene	4.741×10^5	2.94×10^4	4.386×10^5	1.738×10^4	4.369×10^5	2.622×10^4
α-pinene	7.142×10^5	6.31×10^4	6.566×10^5	2.828×10^4	6.354×10^5	2.816×10^4
mesitylene	1.020×10^6	1.02×10^5	9.371×10^5	4.553×10^4	9.262×10^5	5.381×10^4
d-limonene	1.687×10^6	1.21×10^5	1.565×10^6	6.302×10^4	1.511×10^6	4.513×10^4
n-undecane	4.086×10^6	2.48×10^5	3.846×10^6	1.505×10^5	3.675×10^6	1.043×10^5

B

	pooled S			*t*-test A/B		*t*-test B/C		*t*-test A/C	
	fibers A and B	fibers B and C	fibers A and C	*t*-value	pass or fail	*t*-value	pass or fail	*t*-value	pass or fail
n-pentane	1.62×10^3	1.23×10^3	1.53×10^3	1.971	pass	0.320	pass	2.346	pass
n-hexane	1.56×10^3	1.81×10^3	1.89×10^3	2.170	pass	0.909	pass	0.917	pass
benzene	2.54×10^3	1.93×10^3	2.52×10^3	2.273	pass	0.948	pass	3.010	fail
toluene	6.52×10^3	3.02×10^3	6.70×10^3	1.853	pass	3.500	fail	3.381	fail
ethylbenzene	1.77×10^4	1.25×10^4	1.62×10^4	2.209	pass	1.054	pass	3.217	fail
p-xylene	2.04×10^4	1.28×10^4	1.80×10^4	2.091	pass	1.478	pass	3.415	fail
o-xylene	2.41×10^4	2.22×10^4	2.78×10^4	2.081	pass	0.109	pass	1.891	pass
α-pinene	4.89×10^4	2.82×10^4	4.89×10^4	1.666	pass	1.064	pass	2.282	pass
mesitylene	7.88×10^4	4.98×10^4	8.14×10^4	1.480	pass	0.310	pass	1.624	pass
d-limonene	9.63×10^4	5.48×10^4	9.11×10^4	1.804	pass	1.389	pass	2.741	fail
n-undecane	2.05×10^5	1.29×10^5	1.90×10^5	1.660	pass	1.867	pass	3.063	fail

C

	pooled S			*t*-test A/B		*t*-test B/C		*t*-test A/C	
	fibers A and B	fibers B and C	fibers A and C	*t*-value	pass or fail	*t*-value	pass or fail	*t*-value	pass or fail
n-pentane	1.62×10^3	1.23×10^3	1.53×10^3	1.971	pass	0.339	pass	1.818	pass
n-hexane	1.56×10^3	1.81×10^3	1.89×10^3	2.170	pass	0.909	pass	0.917	pass
benzene	2.54×10^3	1.93×10^3	2.52×10^3	2.273	pass	0.966	pass	1.548	pass
toluene	6.52×10^3	3.02×10^3	6.70×10^3	1.853	pass	0.026	pass	1.791	pass
ethylbenzene	1.77×10^4	1.25×10^4	1.62×10^4	2.209	pass	1.058	pass	1.588	pass
p-xylene	2.04×10^4	1.28×10^4	1.80×10^4	2.091	pass	0.780	pass	1.809	pass
o-xylene	2.41×10^4	2.22×10^4	2.78×10^4	2.081	pass	1.558	pass	0.559	pass
α-pinene	4.89×10^4	2.82×10^4	4.89×10^4	1.666	pass	0.847	pass	1.178	pass
mesitylene	7.88×10^4	4.98×10^4	8.14×10^4	1.480	pass	1.266	pass	0.658	pass
d-limonene	9.63×10^4	5.48×10^4	9.11×10^4	1.804	pass	0.950	pass	1.33	pass
n-undecane	2.05×10^5	1.29×10^5	1.90×10^5	1.660	pass	0.541	pass	1.422	pass

[a] (A) represents the data obtained for each of the fibers (17 μg/L at 298 K, 100 μm PDMS). In (B) are the *t*-test comparisons without correction for fiber length. Table C are the *t*-test comparisons after the area counts obtained with fiber C were adjusted upwards by 6% to normalize it to the fiber lengths for (A) and (B).

1 min active grab sample with a charcoal tube at maximum air sampling flow rate for a total volume of 200 mL yields a detection limit of 50 μg/L for pentane and 5 μg/L for toluene compared to 5.5 and 0.4 μg/L, respectively, by SPME for the same 1 min sampling session. Therefore, SPME would provide significantly better detection limits for grab sampling compared to charcoal and can be further ameliorated with lower sampling temperatures, modifications to the length and/or thickness of the fiber, alterations to the coating properties yielding more specific fiber coatings, and use of detectors more responsive to the analytes of interest.

Humidity Effects at Different Temperatures for PDMS. Table 4B summarizes the results from the study of humidity effects on the mass uptake by the fiber. The data indicate there is an ~10% lower mass loading at greater than 90% RH at the temperatures studied. This observation is consistent with other work.[11] The temperatures studied were 290, 298, and 310 K with relative humidities of 0, 30, 50, 70, and 95%. The data suggest that high humidity (greater than 90% RH) interferes in the analyte mass uptake due to adsorption of water by the fiber, thus possibly changing the fiber's characteristics; however, preliminary studies have indicated this is an artifact of injection and could be fully corrected by simply turning off the septum purge gas (data not shown). This is due to the adsorbed or capillary condensed water back-flushing in the hot injector temperature in the extremely narrow bore insert, taking with it a percentage of the absorbed analytes. This is currently under further investigation. It should be emphasized that, for practical purposes, most ambient air measurements occur with relative humidities ranging from 30 to 80% and only occasionally are relative humidities greater than 90% observed, in which case a focus must be placed on this issue.

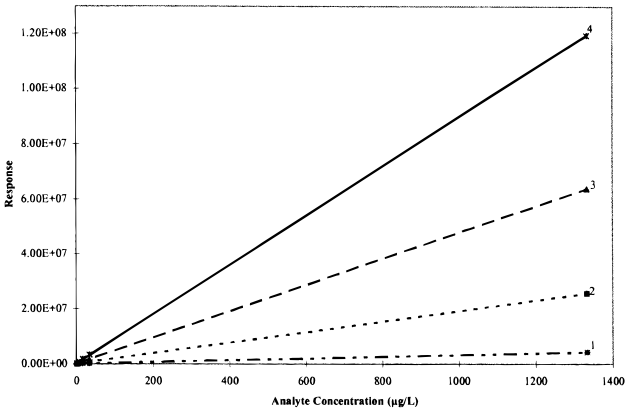

Figure 5. PDMS (100 μm) calibration curves for (1) benzene, (2) ethylbenzene, (3) α-pinene, and (4) *d*-limonene for the concentration range from 0.60 to 1333 μg/L at 298 K.

Table 7. Industrial Concentrations of Styrene (μg/L) Using Different Methods of Field Sampling, Comparing PDMS to Active Sampling with Charcoal, Passive Badge Sampling, and an Active Sampling Portable Photoionization Detector (PID)[a]

sample type	SPME with PDMS	charcoal tube	passive badge (for the sample time)	PID
5 min sample	130	97	90	50−250
30 min integrated	56	54	72	NA[b]

[a] The data in the first column represent the observed concentration of styrene with SPME 100 μm PDMS at 296 K and 25% RH for both grab sampling and integrated sampling. [b] Not applicable.

Field Sampling with SPME Using PDMS. Table 7 summarizes the results from an air sampling session for styrene at an industry that had indoor levels of styrene as a result of the application of a large quantity of vinyl ester resin. The results show very good agreement for the styrene concentration using 100 μm PDMS fast grab sampling and the charcoal tube samples. For 30 min integrated samples with PDMS, i.e., the same PDMS fiber assembly used in the retracted position,[11] there is excellent agreement between the SPME result and the 30 min charcoal tube results. In this case, there is a first-order rate constant for analyte uptake by the fiber as a function of airborne analyte concentration, i.e., weight$_f$/time × conc. This area is currently under investigation, but it appears to be extremely promising for short-term integrated air sampling of those analytes with PDMS *K* values larger than 1000. These findings indicate air sampling with SPME for fast grab samples and integrated sampling can be a good alternate and/or conjunctive method to active charcoal tube sampling.

CONCLUSIONS

SPME with PDMS can be applied to both rapid and accurate ambient air grab sampling for target analytes if the dependence of *K* on temperature is known. If the relationship between temperature and *K* is not known for an analyte, it can be estimated using the analyte's heat of vaporization combined with its *K* at a specific temperature (see Theory). The relationship between *K* for an analyte between air and PDMS and the Kovat's retention index and/or linear temperature-programmed retention index suggests that retention indexes can be used to calibrate PDMS for air sampling without any experimentation or calibration.[17] Once a *K* and its temperature dependence is established for the analyte of interest, the SPME 30 and/or 100 μm PDMS fibers can be used as supplied from the manufacturer given both temperature and relative humidity are carefully monitored during sampling sessions. Fiber-to-fiber method precision better than 9% RSD is possible with fibers of unequal length. Finally, integrated sampling, which is currently under investigation, and field grab sampling with SPME provide a number of distinct and warranted advantages over traditional sampling techniques and should be further investigated given its simplicity and compatibility with air sampling strategies tending toward more environmentally friendly approaches without a compromise to accuracy.

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APPENDIX

The change in volume of a gas as a function of temperature is established as follows:

$$\frac{P_1V_1}{P_2V_2} = \frac{n_1RT_1}{n_2RT_2}$$

But $P_2 = P_1$, therefore

$$\frac{n_2}{V_2} = \frac{n_1T_1}{V_1T_2} = C_2 = C_1\frac{T_1}{T_2}$$

where C_2 is the analyte air concentration (μg/L) at any temperature T_2 (*K*) and C_1 is the known analyte concentration (μg/L) at T_1 (298 K) (see eq 13).

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