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Air Sampling and Analysis of Volatile Organic Compounds with Solid Phase Microextraction

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ABSTRACT

Solid phase microextraction (SPME) presents many advantages over conventional analytical methods by combining sampling, preconcentration, and direct transfer of the analytes into a standard gas chromatograph (GC). Since its commercial introduction in the early 1990s, SPME has been successfully applied to the sampling and analysis of environmental samples. This paper presents an overview of the current methods for air sampling and analysis with SPME using both grab and time-weighted average (TWA) modes. Methods include total volatile organic compounds (TVOCs), formaldehyde, and several target volatile organic compounds (VOCs). Field sampling data obtained with these methods in indoor air were validated with conventional methods based on sorbent tubes. The advantages and challenges associated with SPME for air sampling are also discussed. SPME is accurate, fast, sensitive, versatile, and cost-efficient, and could serve as a powerful alternative to conventional methods used by the research, industrial, regulatory, and academic communities.

INTRODUCTION

Many conventional methods for airborne hydrocarbon sampling involve drawing air through a sorbent or impinger trap, followed by solvent or thermal desorption into an instrument for detection.[1,2] These methods are only capable of integrated measurement over long time periods, and the equipment is often cumbersome, noisy, costly, non-reusable, and difficult to deploy quickly. In many cases, conventional sampling methods are not applicable to indoor air sampling, particularly in cases where very low detection limits are required. In addition, none of the currently available methods can be used for everything from grab sampling to time-weighted average (TWA) sampling and then be reused.

Solid phase microextraction (SPME) presents many advantages over traditional analytical methods by combining sampling, preconcentration, and the direct transfer of the analytes into a standard gas chromatograph (GC).[3] To date, SPME has been successfully applied in numerous environmental, food, flavor, pheromone, pharmaceutical, clinical, and forensic applications.[4,5] Several research studies have focused on the application of SPME to air sampling and analysis.[6-9] SPME sampling methods have been developed for total volatile organic compounds (TVOCs), formaldehyde, and volatile organic sulfur compounds in air.[10-13] SPME can also be interfaced with conventional autosamplers for continuous volatile organic compound (VOC) sampling and analysis of a moving air stream.[14] Two studies have indicated that SPME may also be used for TWA sampling.[15,16]

SPME has been applied to indoor air surveys with fast, portable GCs.[17,18] Initial research has been completed for the application of SPME to aerosol particulate matter sampling and to single-particle analysis.[17,19] Most recently, a novel methodology for rapid air sampling with solid SPME fibers was developed and tested.[20,21] The major advantages of SPME are summarized and compared with sorbent tube methods in Table 1.[3,4] This paper gives an overview of SPME technology and how it can be applied to air sampling and analysis with SPME. Theoretical background for each method is illustrated with field sampling data for indoor air. SPME devices and fibers were used for the method development, sampling, and quantitative analysis of target VOCs,

IMPLICATIONS

SPME is the method of choice in many applications where very sensitive yet simple air sampling and analysis methods are needed. SPME is easy to automate and may eventually replace many labor- and cost-intensive purge-and-trap methods currently used by regulatory agencies, research or academic institutions, and contract laboratories. Besides a routine laboratory analysis, SPME can also be used in field air sampling and on-site analysis. The on-site analysis with SPME allows for immediate assessment of sampled air, increases sample throughput, does not require sample preservation, and allows "hot spot" sampling for many analytes. In addition, it offers the flexibility to conduct grab and TWA sampling at low concentrations that are not attainable by many conventional methods or by the portable analyzer.

Table 1. Comparison of characteristics of SPME with sorbent tubes sampling and analysis.

Characteristic	SPME	Sorbent Tubes
Sampling pumps	No	Yes
Reusable	Yes	No
Cost per sample	Low	High
Grab air sampling mode	Yes	No
TWA sampling mode	Yes	Yes
TVOC analysis	Yes	Yes
Selective sampling for target analyte(s)	Yes	Yes
High sensitivity	Yes	No[a]
Solvent extraction	No	Yes
Analysis with conventional chromatography	Yes	Yes
Sample and analysis cycle	Short[b]	Long
Automated sampling and analysis	Yes	Yes[c]

[a]For many methods; [b]For grab-sampling mode; [c]For analysis only.

TVOCs, and formaldehyde in air. Exposed and retracted SPME fibers were used for grab and TWA sampling, respectively.

SOLID PHASE MICROEXTRACTION DEVICES AND GAS CHROMATOGRAPHY

SPME Device

There are two basic components to the SPME device: the SPME holder and the SPME fiber assembly. The fiber assembly includes the extracting polymer coated on a fused silica fiber that is housed in a needle (Figure 1). The length of the fiber coating is typically 10 mm, with the polymer thickness ranging from 7 to 100 μm.[4] The SPME holder is used to guide the polymer into and out of the needle. The needle serves three purposes: first, to protect the SPME fiber coating, or to preserve extracted analytes; second, to provide a mechanism to introduce the fiber into a chromatographic injector interface (i.e., pierce the septum), and third, to act as a diffusion path length when the SPME device is used for TWA and long-term sampling.[15,16]

There are currently 8 coatings available, including poly(dimethylsiloxane) (PDMS), PDMS/divinylbenzene (PDMS/DVB), and Carboxen/PDMS, which are most popular for air or headspace sampling applications.[4,5] The PDMS coating is a nonporous, amorphous polymeric phase, while the latter two can be considered predominantly porous polymeric phases. Analyte uptake on PDMS is via absorption, while it is adsorptive for PDMS/DVB and likely capillary condensation for Carboxen/PDMS. Although all analytes in air will partition with the polymeric phase, each coating has a different sensitivity and can be used to provide selective air sampling of a particular group or range of analytes, for example, polar or non-polar, semi-VOCs or VOCs.

Grab versus Time-Weighted Average Sampling

There are two modes, or fiber positions, in which air sampling with SPME can take place. The first mode is termed "exposed" fiber sampling, and the fiber is outside of the needle (see Figure 1). The second mode is termed "retracted" fiber sampling, and the fiber is inside the needle. The latter is used for long-term sampling, while the former is used for grab sampling.

Gas Chromatography with SPME

After SPME sampling, the fiber is pulled inside the needle and then either transferred immediately into the injector of a gas chromatograph (Figure 2) or capped and placed inside a cooler for later analysis in the laboratory. During the analysis, the needle is inserted into the heated GC injector, where the SPME fiber coating is exposed to the hot carrier gas and completely desorbed. Complete desorption is fast, requiring no longer than a few seconds for most VOCs, although desorption time may be longer for analytes with higher boiling points. However, desorption times are typically not longer than 1 min for semi-VOCs. After the GC injection/desorption step, the SPME fiber is ready to be used again, that is, the coating is fully desorbed and clean. It should be emphasized that in contrast to many conventional sampling methods based on sorbent tubes or whole air sampling, all of the sorbed (or extracted) analytes are subsequently desorbed and analyzed. As a result, SPME provides the enhancement of sensitivity and eliminates errors associated with sample preparation. The SPME approach presents a significant advantage over conventional sampling methods. The overall quality of chromatographic analysis is improved due to a very narrow band of analyte injection, better resolution, shorter analysis times, higher sample throughput, and no need for coolants. In addition, no solvent is used with SPME; therefore, no background noise and no additional peaks from the solvent are possible.

THEORY OF AIR SAMPLING WITH SOLID PHASE MICROEXTRACTION

Method development for air sampling with SPME involves finding an appropriate fiber coating, an appropriate sampling time, a separation instrument, and a detector. The methods described below are applicable to airborne VOCs (including halogenated VOCs), semi-VOCs, and aldehydes. Methods for other classes of compounds that are not specifically listed in this paper can be found in the literature or modified from the existing headspace or direct extraction methods that were developed for water analysis.[4]

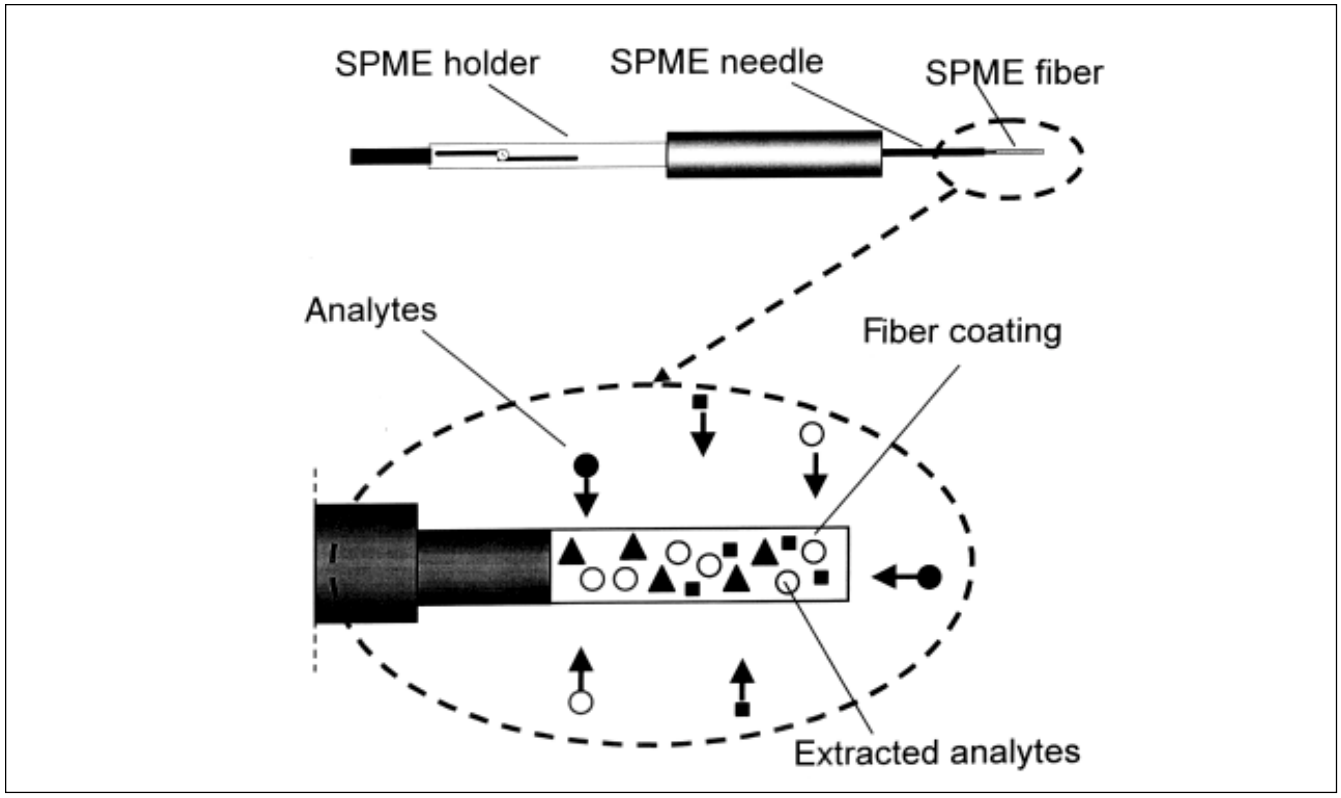

Figure 1. SPME device (fiber coating is exposed to airborne analytes).

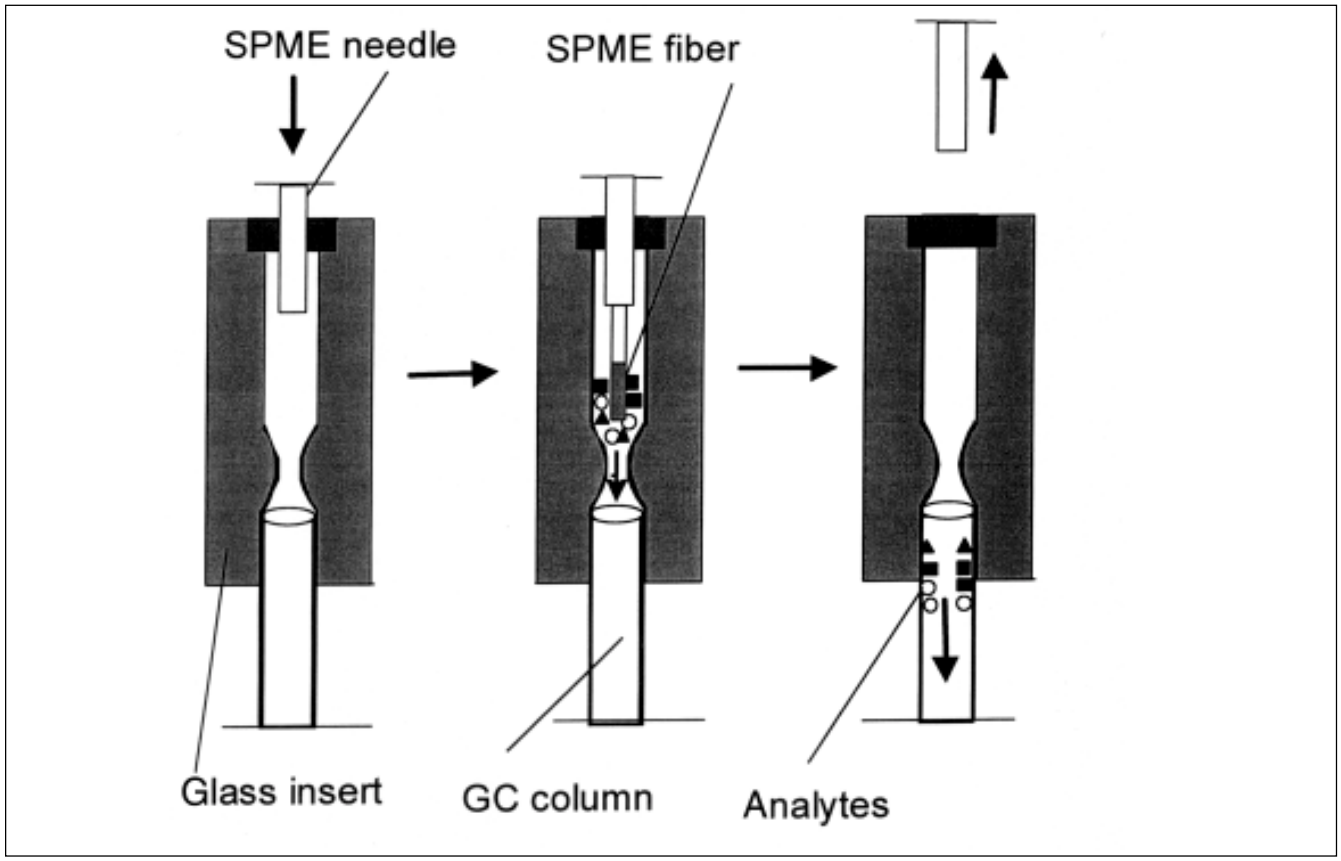

Figure 2. SPME fiber desorption inside a GC injector.

Volatile Organic Compound and Semi-Volatile Organic Compound Sampling with Absorptive Coatings

Air sampling with SPME can be considered as a two-phase system, where the analytes in air (gas-phase) partition to the SPME fiber coating (liquid or solid phase) (see Figure 1). Most of the hydrocarbons in air have a high affinity and partition coefficient for the SPME fiber coating. This partition coefficient is different for each analyte and depends on both the coating type and the analyte physicochemical properties. During SPME sampling, all analytes in air will partition into the coating until they reach equilibrium. As a result, analyte concentrations in the SPME coating will be much higher in comparison with their concentrations in the sampled air. For example, the ratio of these concentrations (at equilibrium and room temperature) for absorptive 100-μm PDMS fiber ranges from ~300 for benzene to 3000 for *o*-xylene and 400,000 for tetradecane. This enrichment process corresponds to the preconcentration step in traditional sampling, which is achieved by pumping large volumes of air through a sorbent bed (or liquid).

To date, one of the most widely used SPME fiber coatings is an absorptive 100-μm PDMS. The absorptive coatings can be used for sampling of very complex samples, for example, gasoline vapors, because there is no competition between analytes. With enough exposure time between the two phases, the analytes of interest in sampled air will eventually reach equilibrium. Equilibrium between the PDMS fiber coating and the analytes in the air may be reached within seconds for very volatile compounds and within several hours for semi-volatile compounds. A mass balance for fiber coating and a gas-phase analyte at equilibrium yields eq 1[3]

$$n_f^{\infty} = \frac{K_{fg} V_f V_g C_g}{K_{fg} V_f + V_g} \qquad (1)$$

where n_f^{∞} is the mass loaded onto the 100-μm PDMS fiber coating at equilibrium (M); C_g is the analyte concentration in the gas phase prior to its exposure to PDMS (M/L^3); V_f and V_g are the volumes for the 100-μm PDMS fiber coating and the analyzed gas, respectively (L^3); and K_{fg} is the partition coefficient between the fiber coating and the analyte in air at equilibrium (-).

The experimental values of K_{fg} for 100-μm PDMS fiber coating and numerous analytes including saturated, aromatic, and unsaturated cyclic hydrocarbons have been previously estimated and published elsewhere.[3,11] They can also be estimated through a series of experiments. The $K_{fg}V_f$ term is typically very small considering the volume of the 100-μm SPME coating ($V_f = 626 \times 10^{-9}$ L) and values of K_{fg} ranging from ~10^2 to 10^7 for typical hydrocarbons found in air. Furthermore, in the case of field air sampling, the volume of air (V_g) is typically very large compared with the volume of fiber coating, and it can reasonably assumed that $K_{fg}V_{fg} + V_g \approx V_g$. As a result, eq 1 can be further reduced, and the concentration of an analyte in the air at equilibrium can be estimated using eq 2[3]

$$C_g = \frac{n_f^{\infty}}{V_f} \frac{1}{K_{fg}} \qquad (2)$$

The amount of an analyte (n_f^{∞}) can be determined from GC analysis and detector response factors. A correction for actual sampling temperature (T) should be made when sampling is carried out at temperatures different from those used to establish the K_{fg} listed in the literature (typically 25 °C). The general temperature dependence is presented in eq 3

$$\log K_{fg} = \frac{a}{T} + b \qquad (3)$$

where a and b are constants that can be estimated from physicochemical parameters.[10,11] Thus, SPME with a 100-μm PDMS coating can be used for air sampling at a wide range of air temperatures. The knowledge of K_{fg} at the sampling temperature and the utilization of eq 2 allows for concentration estimations of single analyte in air. A similar approach can be used to estimate concentrations of total VOCs in complex air samples.

Total Volatile Organic Compounds

Equation 2 can be used to estimate the TVOCs by estimating concentrations associated with each peak present in a chromatogram of an unknown air sample. This approach can be used without prior calibration, provided that all analytes within the range of interest are allowed to reach equilibrium. The maximum equilibration time is typically associated with the least volatile analyte within the range of TVOC analytes. An estimate of the equilibration time can be found in the literature, determined experimentally, or estimated from physicochemical properties.[3,4] Values of K_{fg} for each compound can be calculated using a retention index system to identify unknown analytes on the basis of their retention behavior as related to standard compounds, for example, *n*-alkanes[4]

$$LTPRI = 100 \times \left(\frac{t_{r(A)} - t_{r(n)}}{t_{r(n+1)} - t_{r(n)}} \right) + 100 \times n \qquad (4)$$

where *LTPRI* is the linear temperature programmed retention index; $t_{r(A)}$ is the analyte retention time; $t_{r(n)}$ is the retention time of the *n*-alkane eluting directly before $t_{r(A)}$; $t_{r(n+1)}$ is the retention time of the *n*-alkane eluting directly after $t_{r(A)}$; and n is the number of carbon atoms for $t_{r(n)}$. The *LTPRI* value for almost any hydrocarbon can be estimated when its retention time and the retention times of *n*-alkanes are known for the same linear temperature

chromatographic program. The following equation relates the log K_{fg} for 100-μm PDMS in an air system at 25 °C and the retention index for *n*-alkanes ranging from *n*-pentane to *n*-tetradecane (inclusive).[11]

$$\log K_{fg} = 0.0042 \times LTPRI - 0.188 \quad (5)$$

Equation 5 provides a means to estimate K_{fg} values for any airborne organic compound within the carbon range C_5 to C_{14} for a given value of *LTPRI*.

Volatile Organic Compound Sampling with Adsorptive Coatings

Previous research clearly indicated that adsorptive PDMS/DVB coatings are much more efficient in extracting VOCs, particularly at short extraction times and nonequilibrium conditions.[17,18] When very short sampling times are used (<1 min), the SPME coating can be assumed to be a zero sink; the effects of competitive adsorption are minimal enabling mass calibration based on diffusion-controlled extraction and the fastest extraction technique for air sampling.[18,20] An additional enhancement in sensitivity for air sampling is possible when adsorptive SPME fiber coatings are exposed to fast-moving air. This can be accomplished by interfacing the SPME device with a conventional, industrial hygiene sampling pump.[21]

On-Fiber Derivatization: Formaldehyde

Concentrations of airborne formaldehyde can be estimated using a 65-μm PDMS/DVB adsorptive coating and on-fiber derivatization method.[12] The derivatizing agent, water-soluble *o*-(2,3,4,5,6-) pentafluorobenzyl hydroxylamine (PFBHA), is loaded on the fiber for several minutes using headspace extraction prior to formaldehyde sampling. During actual sampling, the airborne formaldehyde reacts with PFBHA loaded on the fiber, forming a relatively stable formaldehyde-PFBHA oxime. This oxime will remain on the fiber until the analysis. Typical sample preservation consists of capping the needle opening with a narrow-bore Teflon cap to prevent the formaldehyde in air from contacting the coating and to stop the derivatization reaction. The on-fiber reaction is the rate-controlling step, and the amount of oxime formed is proportional to the formaldehyde concentration in air. After the SPME sampling, a conventional GC/flame ionization detector (FID) is then used to determine the amount of formaldehyde-PFBHA oxime formed. This method has reported detection limits of less than 5 ppb and is applicable to routine indoor air sampling for formaldehyde where typical concentrations range from 10 to 50 ppb. The approach described above could be used for sampling and analysis of acetaldehyde and other airborne aldehydes. A similar derivatization step (with a different derivatizing agent) is also used in sorbent tube sampling using the National Institute for Occupational Safety and Health (NIOSH)-2541 method.[1] Another alternative is an impinger method with absorbance spectrophotometry detection.[1]

Time-Weighted Average Sampling

SPME can also be used for long-term integrated or TWA sampling by keeping the fiber retracted inside the needle (Figure 3).[15] In this case, the distance between the fiber opening and the fiber tip serves as the diffusion path. As a result, the sampling (extraction) rate is reduced compared with the exposed fiber, allowing for significant extension of the sampling time. It is assumed that for SPME TWA sampling, the sorbent is a zero sink and the analyte concentration at the opening of the sampling device (needle) is equal to the bulk concentration of analyte (see Figure 3). It must be emphasized that TWA sampling is nonequilibrium sampling, since the SPME sorbent has to remain a zero sink throughout the sampling session. This is assured if the maximum amounts of analytes extracted on the fiber remain below 5–10% of their equilibrium amounts.[12,16] As a result, the sampling rate is not affected and remains a first-order "uptake" rate.

It has been shown that the amount of analyte on the sorbent (n_f) is proportional to the integrated gas-phase concentration over the sampling time (t), gas-phase molecular diffusion coefficient (D_g) (cm²/sec), and the ratio of the needle opening area (A) to the diffusion path length (Z) (eq 6).[11]

$$n_f = D_g \frac{A}{Z} \int C_g(t)dt \quad (6)$$

The value D_g for the analyte of interest can be estimated from physicochemical properties. Equation 6 can be used for the estimation of TWA concentration since n_f can be established from the GC/FID response and t is measured. The diffusion path length can be reduced or increased, providing the flexibility of extending or reducing the sampling time in the field, based on the estimate of an analyte concentration from a fast, "screening" sample with an exposed fiber. Thus, the use of SPME devices for TWA sampling presents the potential user with great flexibility in choosing a time appropriate for both short- and long-term sampling. In comparison, conventional methods require processes that cannot be reused and provide very limited flexibility for grab sampling.

In this research, a commercial SPME holder was modified for TWA sampling (Figure 4). Six additional notches were made in the existing Z-slot. These notches were spaced 5 mm apart to allow for precise retraction of the SPME fibers, thereby controlling the diffusion path inside the SPME needle from 0 to 30 mm. An additional

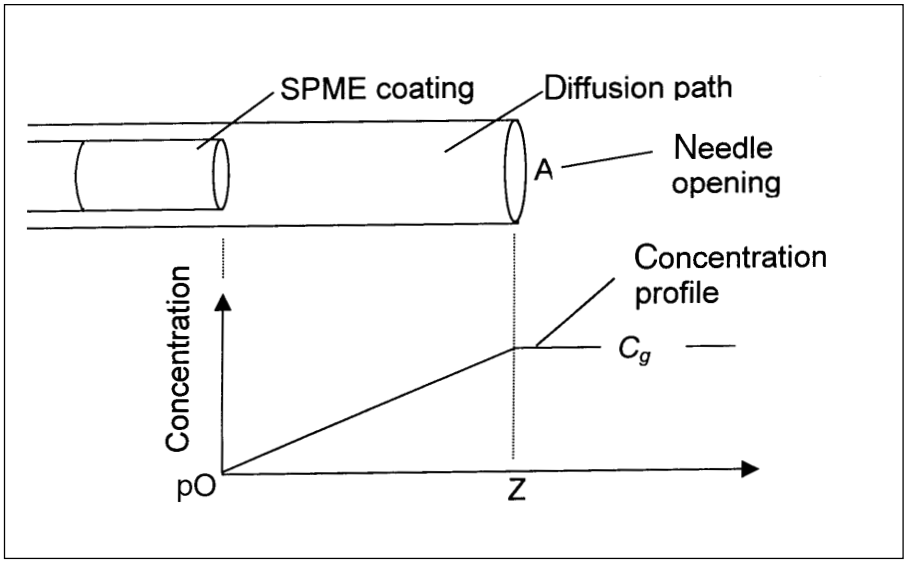

Figure 3. TWA sampling with SPME (fiber coating retracted inside the needle).

notch was placed at the end of the existing Z-slot to enable fiber exposure during GC injection. In addition, the plunger-retaining screw was moved and the tensioning spring on the SPME fiber assembly was removed to accommodate full retraction of the SPME fiber to 30 mm.

METHODS DEVELOPMENT

Laboratory Studies

Standard gas concentrations for target VOCs (including benzene, toluene, ethylbenzene, and *p*-xylene (BTEX) and hexane) were sampled with the adsorptive PDMS/DVB fibers. Calibration curves were developed for the 1-min sampling and were based on the photoionization detector (PID) response to standard gas mixtures. Samples were analyzed immediately using the mobile sampling system described in the "Portable Gas Chromatograph" section. Method detection limits were 1.9, 1.3, 1.6, 1.7, and 8.6 ppb for benzene, toluene, ethylbenzene, xylene, and hexanes respectively. The PDMS 100-μm fiber was used for sampling of TVOCs. The sampling time was generally longer than 1 hr so that equilibrium could be reached between semi-VOCs and the fiber coating. Formaldehyde sampling was conducted with the PDMS/DVB coating and on-fiber derivatization. A 2-min headspace loading of the PFBHA (derivatizing agent) was completed in the field immediately before each sample collection. A 10-min exposure period for grab sampling was used. For the TWA sampling, the SPME fiber was retracted inside the needle from 10 to 30 mm with 2–7 hr sampling times.

Validation with NIOSH Methods

Whenever possible, the SPME method was compared with the standard NIOSH method.[1] For laboratory experiments and the field sampling, ORBO charcoal tubes and personal

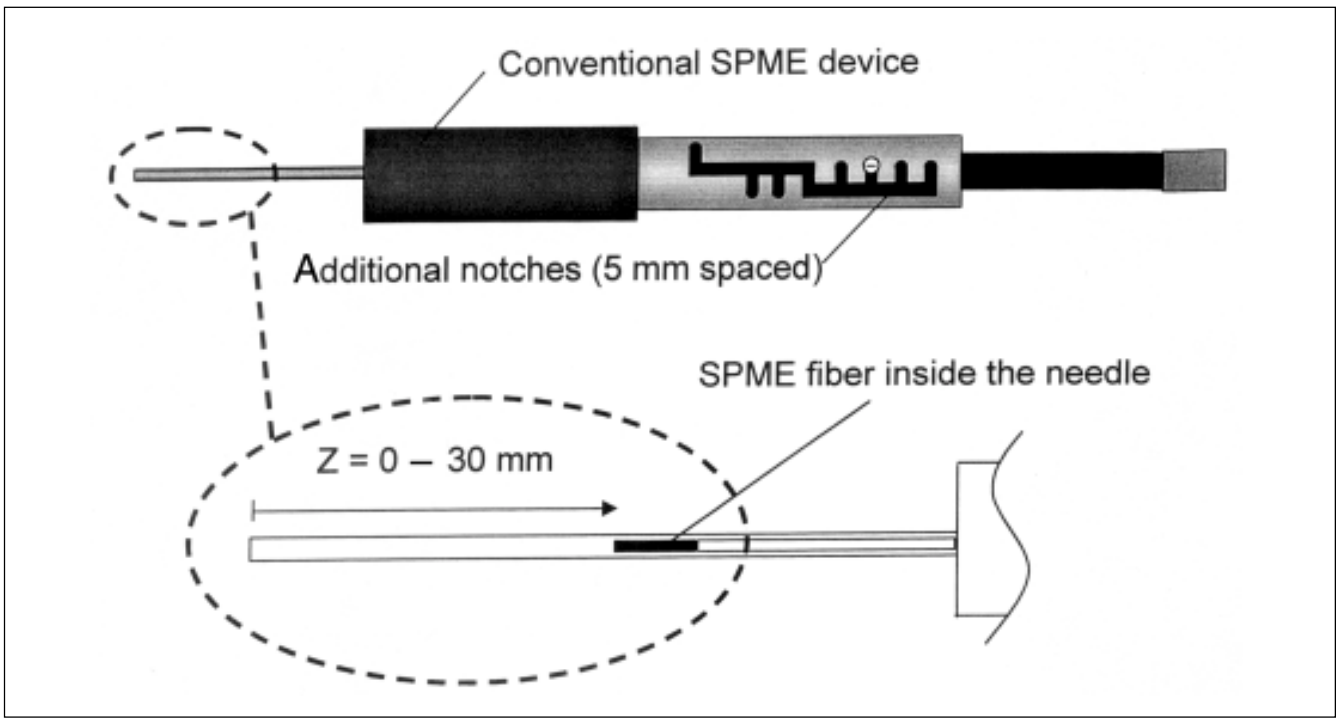

Figure 4. Modified SPME device for TWA sampling.

Table 2. Comparison of target VOC concentrations in standard air (in ppb) measured using 65-μm PDMS/DVB and charcoal tubes.[18]

	Benzene		Toluene		Ethylbenzene		p-Xylene	
	SPME	NIOSH	SPME	NIOSH	SPME	NIOSH	SPME	NIOSH
Measured Avg.	62	62	19	18	4.7	5.2	3.8	4.0
Std. Deviation	1.0	3.1	0.7	1.1	0.2	0.4	0.2	0.7
RSD (%)	1.6	5.0	3.8	6.3	3.9	7.1	4.8	19
Theoretical[a]	64		21	4.1	4.8			

Note: The SPME and NIOSH values are based on $n = 5$ samples. Sampling time for SPME = 1 min; sampling time for the NIOSH-1501 = 2 hr; [a]Based on permeation rates and measured air flow rates.

industrial hygiene (I.H.) pumps (A.P. Buck) were used. Table 2 compares the target VOC concentrations obtained from a parallel air sampling using the SPME and NIOSH methods. The measured concentrations of target VOCs in the standard gas mixtures using both methods are close to each other and to the standard gas concentrations. The results in Table 2 also indicate that the reproducibility of the SPME method was generally better than that of the conventional charcoal tube method. This is generally true for all SPME methods for air sampling.

Field Sampling

Portable Gas Chromatograph. An SRI 8610C portable gas chromatograph (SRI Instruments) was used for immediate on-site analysis of SPME samples. This approach eliminated the need for sample preservation and potential losses of analytes during storage. The GC was equipped with three detectors in series: a PID, an FID, and a dry electrolytic conductivity detector (DELCD). The PID was extremely sensitive to BTEX and was selected for VOC calibration. Both the FID and the DELCD were used to confirm the speciation of target VOCs based on their selective sensitivity to other pollutants present in the same air sample. The field sampling and analysis equipment was assembled on a utility cart to provide mobility in the field. This system consisted of a portable GC, a computer, SPME devices, SPME fiber conditioner, carrier gases, and several personal air pumps.[17,18,23] This sampling system allowed for quick, on-site assembly and transportation by a van or small pickup truck. The compact GC was equipped with a 50-m × 0.2-mm × 0.5-μm film thickness column recommended for the analysis of paraffins, olefins, naphthalenes, and aromatic compounds (Hewlett-Packard). The column temperature program consisted of an initial temperature of 30 °C, followed by ramping at 15 °C/min to 250 °C. The desorption time in the fast SPME injector was 30 sec. The injector consists of a microvolume stainless steel tube heated by a capacitance discharge heater. Once an SPME fiber was inserted into the cold (~30 °C) GC injector, the injector was immediately heated to 200 °C in a few milliseconds. Ultrahigh- purity hydrogen was used as a carrier gas at 45 psi and 4 mL/min flow rate.

Sample Preservation

The alternative approach to sample preservation and later analysis in the laboratory was used for the TVOC, TWA, and formaldehyde air sampling. A previous study indicated that it is possible to preserve an SPME sample over longer periods of time, depending on the SPME coating and the analytes of interest.[24] In this research, a similar approach was used. SPME fibers were retracted ~10 mm inside the needle, sealed with a Teflon narrow-bore cap, and placed on a bed of dry ice (at approximately –20 °C) before sample analysis (Figure 5). Such a cap can be easily made using a solid 1/4-in. Teflon rod and a small drill. Teflon plugs can be periodically cleaned by a combination of sonication in solvents and thermal desorption at high temperature (up to 250 °C) to assure that the plugs are not carrying over contaminants. The preservation technique described above worked very well for adsorptive coatings for both VOCs and formaldehyde as well as the absorptive PDMS coating for semi-VOCs. This preservation technique was selected based on the results of sample preservation experiments.

Table 3 summarizes the results of a sample preservation study that was completed for a wide range of airborne VOCs and semi-VOCs using a 100-μm PDMS fiber coating. Several sample preservation methods were compared, such as both capping and not capping the SPME needles as well as the use of a needle cap combined with storage on a dry ice bed. The percent of sample loss was estimated based on the comparison of each analyte mass detected immediately after sample collection, preservation, and detection. A standard gas mixture of *n*-alkanes from pentane to pentadecane was used. Although this mixture was not representative of a typical indoor air sample, the results can serve as a general guide for typical airborne hydrocarbons with identical carbon number.

A 100-μm PDMS coating was exposed for 30 min to the standard gas mixture and then analyzed immediately. The same fiber was exposed again to the same standard gas mixture for 30 min and then retracted and left either at room temperature or on a bed of dry ice for different storage times before analysis. The second step was repeated

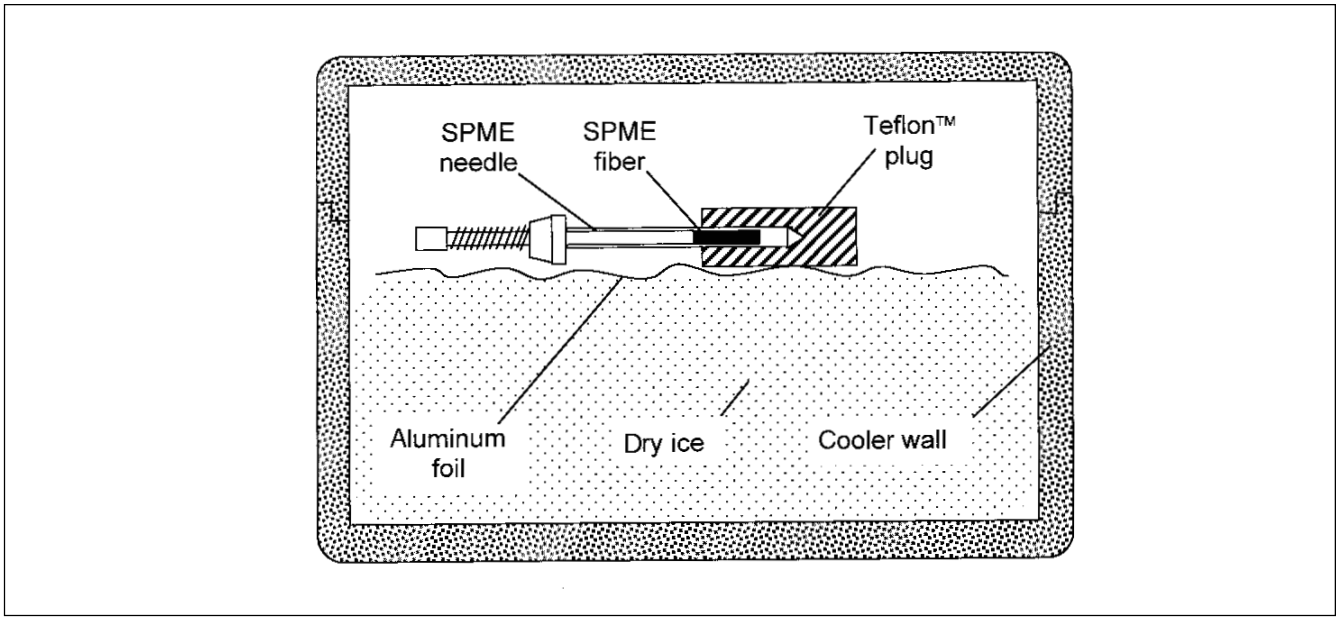

Figure 5. Sample preservation for field SPME sampling.

with and without capping the fiber with a Teflon cap. It can be concluded from Table 3 that the 100-μm PDMS coating was very efficient at retaining semi-VOCs, even without special sample preservation steps. However, addition of the SPME needle capping and storage in low temperature improved the retention of VOCs. As a result, no significant, that is, >5%, loss was observed for all *n*-alkanes within the first 30 min.

At the storage time of 20 hr, the greatest sample loss of 26% was observed for pentane, that is, the most volatile analyte in the standard, and no significant sample loss occurred for dodecane and other semi-VOCs. The results indicate that the SPME needle cap and cold storage can be used for sample preservation for compounds with a carbon number between 5 and 15 and storage time up to ~1 day. Special care should be exercised when the air sample contains very volatile analytes. In this case, extended storage is not recommended for quantitative analysis. Other fiber coatings, for example, adsorptive PDMS/DVB and Carboxen/PDMS, are much more efficient than the absorptive PDMS coating is in retaining very volatile analytes.

Table 3. Comparison of percent sample loss (in %) for sample preservation techniques used for VOC and semi-VOC sampling with 100-μm PDMS fiber coating.

Carbon Number for *n*-Alkane	After 30 Min Uncapped (Room Temp)	After 30 Min Capped (Room Temp)	After 20 Hr Capped (Room Temp)	After 30 Min Capped (Dry Ice Bed)	After 20 Hr Capped (Dry Ice Bed)
C_5	100	13	81	<5	26
C_6	82	15	81	<5	24
C_7	83	14	88	<5	16
C_8	52	14	64	<5	17
C_9	30	16	48	<5	15
C_{10}	19	16	40	<5	14
C_{11}	13	16	36	<5	10
C_{12}	11	14	35	<5	<5
C_{13}	<5	<5	32	<5	<5
C_{14}	<5	<5	30	<5	<5
C_{15}	<5	<5	14	<5	<5

Note: Results based on $n = 1$ sample.

Laboratory Gas Chromatography

All TVOC analyses were performed on a Varian GC 3400 gas chromatograph (Varian Associates) equipped with a 30 m × 0.25 mm, 1-μm film DB-5 column (J&W Scientific), and a septum-equipped programmable injector with a narrow SPME glass insert. Ultrahigh purity(UHP) helium was used as carrier gas at 20-psi head pressure. The column temperature program used was 50 °C, held for 1 min, then a ramp of 15 °C/min to 230 °C, held for 5 min. The injector temperature was 250 °C, and the coating desorption time was extended to 5 min. All formaldehyde analysis was performed on the same kind of GC and column. The GC oven temperature was programmed from 45 °C (held

for 2 min) to 200 °C at a ramp of 30 °C/min, followed by a ramp of 50 °C/min to 290 °C and held for 4 min. The SPI injector was set to 210 °C, and the detector temperature was set to 300 °C. The carrier gas was UHP hydrogen at 26-psi pressure and an initial linear flow velocity of 106 cm/sec.

RESULTS

Total Volatile Organic Compounds

Figure 6 presents a comparison of typical chromatograms obtained simultaneously by the sorbent tube and SPME sampling with 100-μm PDMS coating. The chromatograms shown present an air sample collected in a bathroom of a residential apartment during vigorous cleansing with a number of commercial bathroom cleaning products. Sampling time was 60 min for SPME and 3 hr for the charcoal tube at a 500-mL/min sampling rate. This sampling time was selected to ensure that semi-VOCs up to dodecane could reach equilibrium with the SPME coating and that there would be enough mass sorbed on the charcoal tube.

It can be concluded from Figure 6 that the sampling of very volatile compounds with the 100-μm PDMS coating suffers from a low preconcentration (relatively low K_{fg}) and the possibility of significant sample loss over extended preservation times. Similarly, many semi-VOCs were not detected with charcoal tubes. In addition, the typical number of analytes detected by SPME was usually at least an order of magnitude larger than the number of analytes detected with charcoal tubes. Therefore, for comparison of the two methods, the data analysis was restricted to compounds that have retention times between octane and dodecane, that is, analytes that were detected by both methods. However, it should be emphasized that this sampling range is not optimal for sorbent tubes. Such an artificial data range selection was possible because the use of *n*-alkane standards allows for comparison of their retention times with retention times for each unknown peak in an air sample within the selected range.

Table 4 presents TVOC concentrations measured in an indoor air survey for an apartment building and a residential house. Measured concentrations were in the range typical of indoor air concentrations. Concentration estimates by SPME and charcoal sampling were also comparable. It should be emphasized that differences in measured concentrations via the PDMS coating and the charcoal sorbent tubes are due to the differences in the sensitivity of the target TVOC range associated with the two methods, differences in sampling time, and possible changes in VOC concentrations over the sampling

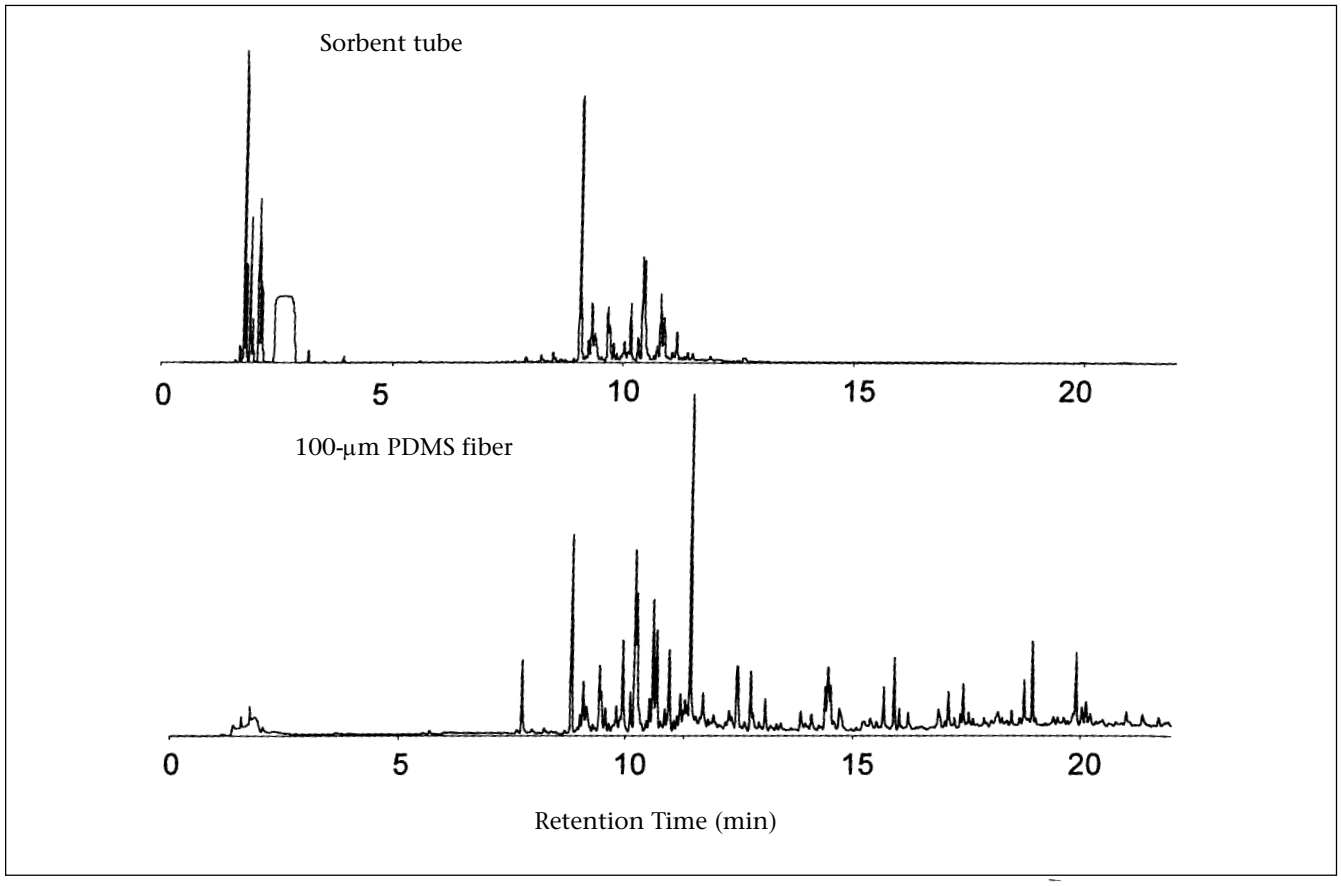

Figure 6. Comparison of chromatograms of an indoor air sample collected in a bathroom of a residential apartment during cleaning with typical bathroom cleaning products.

Table 4. Comparison of TVOC concentrations in the C_8–C_{12} range during indoor air survey.

Site	Room	Sampling Temperature (°C)	SPME (μg/L)[a]	NIOSH-1550 (μg/L)[a]
Rental apartment	Bathroom	28	2.3	2.9
	Kitchen	27.5	1.7	1.1
Residential house	Garage	24	0.5	0.5

Note: Sampling time for SPME = 120 min; Sampling time for the NIOSH-1550 = 2.5 hr; [a]Adjusted for sampling temperature and pressure.

period. If the analyte concentration was constant over the sampling period (which is not feasible in the field), equilibrium would be established between the air and the PDMS fiber for a given analyte. This equilibrium would be disrupted if the concentration of the analyte decreased or increased. For example, if the air concentration was high in the first 30 min of sampling and then dropped, the analytes would start to re-equilibrate to the new concentration (eq 2).

The time needed to re-equilibrate depends on the physicochemical parameters of the analyte. While it takes less than 1 min for pentane, it takes ~2 hr for dodecane. Another reason for discrepancies may be the changes in sampling temperature. This change in temperature affects the pump flow rate significantly, which in turn introduces a significant error in the amount of air forced through the charcoal tubes. Laboratory studies showed that the relative standard deviation for the NIOSH-1550 method ranged from 16 to 41% for C5–C15 *n*-alkanes, compared with 2–6% for the 100-μm PDMS coating. Therefore, it is highly possible for NIOSH-based field sampling results to be within 40% of the true concentration value.

Target Volatile Organic Compounds

The VOC concentration change effect can be minimized when fast air sampling with adsorptive SPME coatings is used. Measured concentrations of target VOCs inside the engineering shop and plant operations with the PDMS/DVB 65-μm coating and 1 min of sampling time are summarized in Tables 5 and 6. Target VOC concentrations obtained by the SPME and the NIOSH methods were comparable and ranged from the low ppb to low ppm range. In most cases, the highest concentration detected was associated with toluene. Ambient concentrations of target analytes were typically below the method detection limits. SPME coupled to a portable GC allowed for monitoring of concentration changes. For example, in the case of the vehicle shop (see Table 6), large doors left open for a few minutes resulted in a significant drop of target VOC concentrations. The next two samples collected after the door was closed again, that is, samples #2 and #3, show the trend of increasing concentrations, indicating that the source was located in the vehicle shop. Differences in measured concentrations between the two methods were mainly due to VOC concentration variations during sampling events and radically different sampling spans, that is, from 1 min for SPME to several hours for charcoal tubes. In some cases, the instantaneous release of chemicals was also detected in several other locations with the SPME device and a fast, portable GC. In a carpenter shop in plant operations (see Table 6), a sharp increase of *m,p*-xylenes, ethylbenzene, and toluene was detected after a worker used a super glue on a wood table. Decreases in measured VOC concentrations with time were evident in the paint shop (see Table 5), where grab SPME sampling was conducted after a painting event.

Another advantage of coupling fast SPME sampling with portable GC is the possibility of "hot spot" sampling and on-site sampling. This was the case during an indoor air survey conducted in a residential house with unusually high BTEX concentrations.[18] The combination of SPME and fast portable GC made it possible to find the source of contamination in near real-time. This was accomplished by repetitive sample collection in several suspect locations inside the house. It was found that high

Table 5. Summary of target VOC concentrations (in ppb) in the engineering shops.

Room	VOC	SPME 1	SPME 2	SPME Average	NIOSH
Paint shop	Benzene	17	12	15	43
	Toluene	953	656	804	934
	Ethylbenzene	59	37	48	16
	m,p-Xylene	102	15	58	63
	Hexane	468	409	439	352
Grinding shop	Benzene	0.8	1.0	0.9	1.2
	Toluene	39	20	30	24
	Ethylbenzene	6.1	5.3	5.7	6.0
	m,p-Xylene	6.1	6.6	6.3	5.9
	Hexane	71	37	54	44
Carpenter shop (I)	Benzene	12	8.3	10	11
	Toluene	708	491	599	1330
	Ethylbenzene	9.9	11	11	8.5
	m,p-Xylene	6.1	6.6	6.3	23
	Hexane	526	507	517	189

Note: 1 and 2 = first and second SPME sample in each room; Sampling time for SPME = 1 min; Sampling time for the NIOSH-1501 = 2 hr.

levels of target VOCs resulted from a gasoline release, which originated from the vehicle and lawn mower inside the attached garage. On close inspection, it was found that the seal between the garage and the living space was not sufficient to contain the gasoline vapors in the attached garage.

Compared to the conventional charcoal tube method, the SPME air sampling combined with analysis on the portable GC was much faster and simpler. In most cases, the NIOSH method required at least 2 hr sampling followed by 1 hr for CS_2 extraction and GC analysis. NIOSH-1501 can only monitor the average concentration of VOCs in air during a relatively long sampling period. Because the SPME method required neither solvent extraction nor sample preservation, the total time for sampling and analysis of each air sample by the SPME/portable GC method was reduced to an average of 15 min. In cases where there was an instantaneous release of VOCs, the SPME PDMS/DVB fiber was capable of detecting concentration changes associated with the incident. To date, such analyses could be achieved only by very specialized analytical equipment, for example, real-time monitors calibrated to a particular VOC, or online GC with a sophisticated automated sampling interface.

Table 6. Summary of target VOC concentrations (in ppb) at plant operations.

Room	VOC	SPME					NIOSH
		1[a]	1	2	3	Average	
Vehicle shop	Benzene	43	5.3	16	16	12	17
	Toluene	94	17	35	42	31	1 7
	Ethylbenzene	19	2.5	5.1	14	7.2	2.7
	m,p-Xylene	33	1.5	9.9	12	7.9	9.0
	Hexane	4.9	4.9	13	5.3	7.7	12
			1	**2[b]**	**3[b]**		
Carpenter shop (II)	Benzene		3.7	5.3	2.3	3.8	7.8
	Toluene		32	22	9.8	21	9.0
	Ethylbenzene		4.1	36	22	21	2.6
	m,p-Xylene		3.9	4.8	74	28	7.1
	Hexane		86	45	17	49	3.5
Paint shop	Benzene		1.3	2.2	2.4	2.0	4.9
	Toluene		834	523	848	735	976
	Ethylbenzene		200	95	131	142	96
	m,p-Xylene		196	114	170	160	67.3
	Hexane		N/D	N/D	N/D	N/D	N/D
Outdoors	Benzene	D					
Other target analytes below detection limits							

Note: 1, 2, and 3 = first, second, and third SPME sample in each room; D = detected below method detection limits; N/D = not detected; Sampling time for SPME = 1 min; Sampling time for the NIOSH-1501 = 2 hr; [a]Large doors were open after sample was collected and closed before the collection of sample 1; [b]Carpenter was using open glue can during sampling event.

Formaldehyde and Time-Weighted Average Sampling

The summary of formaldehyde analyses by SPME (10-min grab mode and 7-hr TWA mode) and NIOSH-2541 simultaneously is presented in Table 7. Measured formaldehyde concentrations at various locations within plant operations ranged from ~10 to 90 ppb. Higher concentration was recorded in a special case, that is, 90 ppb in a paint shop with a large paint storage area. The concentration measured by the 7-hr TWA mode was in good agreement with the 10-min grab sampling. The SPME-based concentration was close to the NIOSH-based concentration. The outdoor concentrations detected with the SPME device were also consistent with values listed in the literature.[22,23]

Table 7. Summary of formaldehyde concentrations (in ppb) for two indoor air surveys.

Site	Room	NIOSH- 2541	SPME (grab 10 min)	SPME (TWA)
Plant operations	Vehicle shop		44	
	Carpenter shop		11	
	Paint shop	69 (7 hr)	90	83 (7 hr)
	Outdoor air		12	

CONCLUSIONS

The following conclusions stemmed from this study:

(1) Air sampling with SPME devices proved to be a powerful alternative to NIOSH-based field sampling of VOCs, semi-VOCs, and formaldehyde, particularly at very low concentrations for fast, solventless analysis.

(2) SPME-based sampling proved to be reliable for both grab and TWA sampling. The sampling times ranged from 1 min to 7 hr, rendering the SPME device useful for a wide range of exposure assessments.

(3) The PDMS coating was more sensitive to the air sampling of semi-VOCs. This coating was also very efficient in retaining semi-VOCs over long periods of time.

(4) The PDMS/DVB coating was more sensitive to VOCs, particularly at sampling times of less than 1 min, and was also more efficient in retaining VOCs over a longer period of time.

(5) Fast separation and speciation of VOCs common in indoor air environments was possible using a portable GC equipped with PID/FID/DELCD detectors in series.

(6) In all cases, the use of SPME devices allowed for a significant, at least 10-fold, reduction of the total sampling and analysis time. The total sampling and analysis time was less than 15 min in cases in which SPME devices were combined with the use of a fast, portable GC. In this case, monitoring of varying target VOC concentrations is possible.

(7) SPME coupled with portable GC allows for "hot spot" sampling, fast on-site analysis, and immediate remediation of some indoor air pollution problems.

(8) SPME showed good correlation with NIOSH methods in cases where VOC concentrations were greater than NIOSH method detection limits.

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