Air Sampling with Solid Phase Microextraction

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Abstract. Solid phase microextraction (SPME) presents many advantages over conventional analytical methods by combining sampling, pre-concentration and direct transfer of the VOCs into a standard gas chromatography (GC) system. Since its introduction SPME has been applied to the sampling and analysis of environmental samples including airborne VOCs and particulates. The first part of this paper presents theory of air sampling with SPME and an overview of the a few current methods for quantitative air sampling and VOC determination with SPME using grab (‘instantaneous”) and time-weighted average (TWA) modes. The second part of this paper is focused on the recent development of the theory and applications of rapid air sampling and quantification of VOCs in air with adsorptive SPME fiber coating. This approach based on forced and controlled air flow of sampled air and diffusion-based calibration, reduces the effects of VOC competition and displacement. Experiments are currently conducted to apply the rapid SPME sampling method to determination of chemical composition and concentrations of agricultural odors.

Keywords. Air pollution, air quality, air sampling, chromatography, gases, analysis, concentration.

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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. These methods are capable of integrated measurement over long time periods and the equipment is often cumbersome, noisy, costly, often non-reusable and difficult to deploy on a moment notice. Near real-time monitors for a particular gas often suffer from interferences from other gases with similar properties. In many cases, conventional sampling methods are not applicable to sampling of odors and odorous gases, particularly in cases where very low analytical detection limits are required. In addition, none of the currently available methods can be used for everything from grab (“instantaneous”) sampling to time-weighted average (TWA) sampling and then be reused. Solid phase microextraction (SPME) can be considered as an alternative to conventional sampling and sample preparation that addresses these issues.

SPME becomes the method of choice in many applications where very sensitive, yet simple air sampling and analysis methods of complex volatile organic compound (VOC) mixtures in air are needed. SPME presents many advantages over traditional analytical methods by combining sampling, pre-concentration and the direct transfer of the VOCs into a standard gas chromatograph (GC) (Pawliszyn, 1997). The pre-concentration (or “enrichment”) is based on partitioning between air and a SPME polymeric coating.

To date, SPME has been successfully applied in numerous environmental, food, flavor, pheromone, pharmaceutical, clinical and forensic applications (Pawliszyn (ed.), 1999; Scheppers-Wiercinski (ed.), 1999). Increasing number of research studies are focusing on the application of SPME to air sampling and analysis (Chai and Pawliszyn, 1995; Grote and Pawliszyn, 1997; Martos and Pawliszyn, 1997; Eisert et al., 1998, Koziel and Pawliszyn, 2001c). SPME sampling methods have been developed for total volatile organic compounds (TVOCs) (Martos and Pawliszyn, 1997; Martos et al., 1997), formaldehyde (Martos and Pawliszyn, 1998; Koziel et al., 2001), ammonia (Robacker and Bartelt, 1996), and volatile organic sulfur compounds (Wardecki and Namiesnik, 1999) in air. SPME can also be interfaced with conventional autosamplers for continuous VOC sampling and analysis of a moving air stream (Eisert et al., 1998). Several studies indicated that SPME may also be used for time-weighted average (TWA) sampling for long-term sampling (Martos and Pawliszyn, 1999; Khaled and Pawliszyn, 2000; Koziel et al., 2001b). SPME has been applied to indoor air surveys with fast and portable gas chromatography (GC) (Koziel et al., 1999; Jia et al., 2000). Initial research has been completed for the application of SPME to aerosol, particulate matter sampling and a single particle analysis (Koziel et al., 2001a; Odziemkowski et al., 2001). Most recently, a novel methodology for rapid air sampling with solid (adsorptive) SPME fibers was developed and tested (Koziel et al., 2000b; Augusto et al., 2001). The major advantages of SPME are summarized and compared with sorbent tube methods in Table 1 (Koziel and Pawliszyn, 2001).

Some of the SPME disadvantages may be associated with its novelty and the necessity of using models for quantification. These models may not be intuitive as those used for conventional air sampling, and may also require knowledge of several physicochemical parameters, e.g. air-solid phase partition coefficient, gas-phase molecular coefficient. However, these parameters can be found in literature or determined experimentally, as is described in this paper. Another limitation is the fact that the SPME sampling and analysis is usually completed by the same person.

This paper gives an overview of SPME methodology and how it can be applied to air sampling and analysis with SPME. Because much of the theory was/is being published in analytical chemistry literature, more space is devoted to theoretical background to quantitative SPME sampling with absorptive and adsorptive fiber coatings. The experimental part of this paper
focuses on the development and applications of devices for fast field sampling for VOCs with adsorptive SPME coatings.

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

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>SPME</th>
<th>Sorbent Tubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sampling pumps</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Reusable</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Cost per sample</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Grab (&quot;instantaneous&quot;) air sampling mode</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>TWA sampling mode</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>TVOC analysis</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Selective sampling for target analyte(s)</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>High sensitivity</td>
<td>Yes</td>
<td>No(^a)</td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Sample and analysis cycle</td>
<td>Short(^b)</td>
<td>Long</td>
</tr>
<tr>
<td>Automated sampling and analysis</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Note: \(^a\) = depending on analytical methods; \(^b\) = for grab sampling mode.

**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 µm to 100 µm. 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 time-weighted average (TWA) and long-term sampling.

There are currently 8 SPME coatings available, including poly(dimethylsiloxane) (PDMS), PDMS/divinylbenzene (PDMS/DVB) and Carboxen/PDMS, that are most popular for air or headspace sampling applications. The PDMS coating is a non-porous, 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 more selective air sampling of a particular group or range of analytes, e.g., polar or non-polar, semi-VOCs or VOCs.

**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 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. After the GC injection/desorption step, the SPME fiber is ready to be used again, i.e., 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.

**VOC Sampling with Absorptive SPME 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) (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 to their concentrations in the sampled air. This enrichment process corresponds to the pre-concentration 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 coating is an absorptive 100 µm PDMS. The absorptive coatings can be used for sampling of very complex samples e.g., 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 several hours for semi-volatile compounds. A mass balance for fiber coating and a gas-phase analyte at equilibrium, yields eq 1 (Pawliszyń 1997):

\[
n_f^\infty = \frac{K_{fg} V_f V_g C_g}{K_{fg} V_f + V_g}
\]

where \(n_f^\infty\) = mass loaded onto the 100 µm PDMS fiber coating at equilibrium (M); \(C_g\) = analyte concentration in the gas phase prior to its exposure to PDMS (M/L^3); \(V_f\), \(V_g\) = volumes for the 100 µm PDMS fiber coating and the analyzed gas, respectively (L^3); \(K_{fg}\) = 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. 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 approximately a $10^2$ 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 $K_{fg}V_f + V_g \approx V_g$.

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 (Pawliszyn 1997):

$$C_g = \frac{n_f}{V_f} \frac{1}{K_{fg}}$$

(2)

The amount of an analyte ($n_f^{\infty}$), 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 at 25 °C). The general temperature dependence is presented in eq 3.

$$\log K_{fg} = \frac{a}{T} + b$$

(3)

where $a$ and $b$ are constants that can be estimated from physicochemical parameters (Martos and Pawliszyn, 1997; Martos et al., 1997). 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 total volatile organic compounds (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 (Pawliszyn, 1997). 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, e.g., $n$-alkanes (Pawliszyn, 1997):

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

(4)

where $LTPRI = \text{linear temperature programmed retention index}$; $t_{r(A)} = \text{analyte retention time}$; $t_{r(n)} = \text{retention time of the } n\text{-alkane eluting directly before } t_{r(A)}$; $t_{r(n+1)} = \text{retention time of the } n\text{-alkane eluting directly after } t_{r(A)}$; $n = \text{number of carbon atoms for } t_{r(n)}$. 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) (Martos and Pawliszyn, 1997).

$$\log K_{fg} = 0.0042 \times LTPRI - 0.188$$ (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 $LTPRI$.

**VOC Sampling with Adsorptive SPME Coatings**

Previous research clearly indicated that adsorptive PDMS/DVB coatings are much more efficient in extracting VOCs, particularly at short extraction times and non-equilibrium conditions (Jia et al., 2000; Koziel et al. 2000). 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 (Koziel et al. 2000, Augusto et al. 2001).

The solid SPME fiber coating can be modeled as a long cylinder with length $L$, and outside and inside diameters of $b$ and $a$, respectively. When the coating is exposed to moving air, an interface (or boundary layer) with thickness $\delta$ develops between the bulk of air and the idealized surface of the fiber (Figure 3). The analytes are transported from the bulk air to the surface of the coating via molecular diffusion across the boundary layer. In most cases, the molecular diffusion of analytes across the interface is the rate-limiting step in the whole adsorption process.

![Figure 3. Schematic of rapid extraction with adsorptive SPME fiber coating in a cross air flow.](image)

The analyte concentration in the bulk air ($C_g$) can be considered constant when a short sampling time is used, and there is a constant supply of an analyte via convection. The adsorption binding is instantaneous and the analyte concentration on the coating surface ($C_0$) is far from saturation and can be assumed to be negligible for short sampling times and relatively low
analyte concentrations in a typical air. The analyte concentration profile can be assumed to be linear from \( C_g \) to \( C_0 \). Diffusion inside the pores of a solid coating controls mass transfer from \( b \) to \( a \) (Figure 3) (Koziel et al., 2000). The mass of extracted analyte with sampling time can be derived using the analogy of heat transfer in a cylinder with inside and outside diameters of \( b \) and \( \delta \), respectively, with a constant axial supply of heat:

\[
n(t) = \frac{2\pi D_g L}{\ln \left( \frac{b + \delta}{b} \right)} \int_0^t C_g(t) dt
\]

where: \( n \) is the mass of extracted analyte over sampling time (\( t \)) in ng; \( D_g \) is the gas-phase molecular diffusion coefficient (cm\(^2\)/s); \( b \) is the outside radius of the fiber coating (cm); \( L \) is the length of the coated rod (cm); \( \delta \) is the thickness of the boundary layer surrounding the fiber coating (cm); and \( C_g \) is analyte concentration in the bulk air (ng/mL). It can be assumed that the analyte concentration is constant for very short sampling times. Equation 6 can be modified to estimate the analyte concentration in the air in ng/mL for rapid sampling with solid SPME coatings:

\[
C_g = \frac{n \ln \left( \frac{b + \delta}{b} \right)}{2\pi D_g L t}
\]

Values of \( D_g \) for each analyte can be found in the literature or estimated from physicochemical properties (Tucker and Nelken, 1990). The thickness of the boundary layer (\( \delta \)) is a function of sampling conditions. The most important factors affecting \( \delta \) are SPME coating radius, air velocity, air temperature and \( D_g \) for each analyte. The effective thickness of the boundary layer can be estimated using Equation 8, adapted from the heat transfer theory for an SPME fiber in a cross flow (Pawliszyn, 1997):

\[
\delta = 9.52 \frac{b}{Re^{0.62} Sc^{0.38}}
\]

where \( Re \) is the Reynolds number = \( 2u b \nu \); \( u \) is the linear air velocity (cm/s); \( \nu \) is the kinematic viscosity for air (cm\(^2\)/s); \( Sc \) is the Schmidt number = \( \nu / D_g \). Equation 9 indicates that the thickness of the boundary layer will decrease with an increase of the linear air velocity and that the air velocity needs to be controlled for quantification.

Using eqs 7 and 8, the concentration of an analyte can be directly estimated from the chromatographic peak area, given that the sampling conditions (sampling time, air velocity, temperature, and pressure) and constants (diffusion coefficient and fiber dimensions) are known. For that reason, apart from the suppression of inter-analyte effects, this methodology also allows quantification of analytes in air without construction of calibration curves. Another benefit is the increase of the extracted amounts (and therefore, of the sensitivity), when this approach is compared to the traditional “static” SPME sampling (simple exposure of the fiber to the air).

The experimental part of this paper describes a portable device designed to apply the dynamic non-equilibrium SPME sampling concept to analysis of airborne chemicals with adsorptive coatings. The suitability of this approach both for quantification of volatile organic contaminants in indoor air was examined. Also, quantification of air contaminants using dynamic SPME sampling was compared to results obtained using a standard air analysis method.
METHODS DEVELOPMENT

Chemicals & Supplies.

All chemicals were of analytical grade and used as supplied: benzene, toluene, ethylbenzene, o-xylene, p-xylene, and mesitylene (Sigma-Aldrich, Mississauga, ON, Canada) and carbon disulfide (BDH, Toronto, ON, Canada). The SPME holder and 65 µm PDMS/DVB fibers were obtained from Supelco (Oakville, ON, Canada); the fibers were conditioned at 210 °C for 8 h prior to their use. Supelco ORBO-32 charcoal tubes and a Model I.H. portable air pump (A.P. Buck, Orlando, FL) were employed for the validation quantitative analysis according to NIOSH method #1501 (NIOSH, 1994). All preparations involving CS₂ (flammable and toxic) and benzene (suspect carcinogen) were carried out in a ventilated hood.

Gas Chromatography

Air samples were analyzed using a Varian Star 3400 GC-FID chromatograph equipped with a 30 m × 0.25 mm × 0.25 µm Supelco SPB-5 column and SPI; 2.0 mL/min helium at 20 psi was used as carrier gas. The temperatures were set at 250 °C for the FID and 210 °C for the SPI, and the column oven program for all injections was: 1 min hold at 60 °C, followed by a 15 °C/min ramp until ramped to 180 °C and hold there for 3 min.

Portable Dynamic Air Sampling Devices (PDAS) for SPME

A new device for rapid air sampling under dynamic conditions were projected and built; the design concepts for these apparatus are discussed in Results and Discussion below (Augusto et al., 2001). Figure 4 shows the schematics of the device, built using a VS-513F household hair dryer (Helen of Troy, El Paso, TX) modified to revert the air flow direction and to disable the internal heating coil. An aluminum tube was machined and adapted to the front part of the modified hair dryer. Two plain cardboard sheets fixed to the opposite side of the aluminum tubing creating a 3 mm slit; the modified hair dryer suction forces the passage of the ambient air through this slit. PDAS-SPME sampling was performed by exposing the fiber to the flowing air in front of the slit. The average air speed in front of the slit was measured to be 1.5 m/s with an HHF51 digital wire anemometer (Omega Engineering, Stamford, CT). All data presented in this work was collected using this apparatus.

Quantitative Analysis of VOCs in Indoor Air.

PDAS-SPME was employed to quantify aromatic hydrocarbons present in the air of several sites in the University of Waterloo. These sites included two different locations in a chemical lab (close to a solvent storage bin and in an analytical instrument room), Motor Vehicle Maintenance Shop and in the Engineering Mechanical Shop. Replicate measurements exposing the SPME fiber to the flowing air for 30 s were made (Augusto et al., 2001). Uncertainties were expressed as estimates of standard deviation of replicates, i.e., Vehicle and Mechanical Shop air analysis = 3 replicates and Laboratory air analysis = 8 replicates. Concentrations of the aromatic hydrocarbons were calculated using Equation 7 for non-equilibrium dynamic SPME extraction. It was assumed that the thickness of the boundary layer did not significantly change when air velocity was greater than 10 cm/s. Thus, the threshold air velocity of 10 cm/s was used to estimate the thickness of the boundary layer in Equation 8.

For comparison purposes, Vehicle and Mechanical Shop samples were simultaneously analyzed using the NIOSH Method #1501 for aromatic VOCs. Air was pumped through ORBO-32 charcoal adsorption tubes with sampling times and flow rates adjusted according to the level
of contamination of each sample (see Results below). Immediately after the sampling, both the charcoal portion of the tube containing the extracted analytes and the breakthrough control portion were transferred to separated 4 mL glass vials sealed with Teflon-coated silicone septa. Two mL of CS$_2$ were added to each vial. After 1 h 1 µL of the CS$_2$ phase in the vials was injected to the GC-FID system using the same operational conditions employed for the PDAS-SPME analysis (Augusto et al., 2001).

Figure 4. Schematic of the portable device for rapid air sampling with SPME.

RESULTS AND DISCUSSION

Design Aspects of the PDAS-SPME

The PDAS-SPME complements previously described devices for field SPME sampling (Muller et al., 1999). These devices and the techniques used extractions under analyte/fiber equilibrium conditions, which demands the use of calibration curves or quantification based on chromatographic retention data. However, quantification in non-equilibrium conditions, where the analyte uptake depends only on its diffusion through the static boundary layer, has several advantages for field use. Since no calibration procedures are needed for well-defined flow rates, the analytical process is simplified. Also, the sampling time is noticeably shorter when compared to the typical equilibrium times for airborne analytes, resulting in faster analysis. The main design feature of the PDAS-SPME project is to ensure a constant and uniform air flow around the fiber, consistent with the demands of diffusion-based extraction. These devices should also provide flow rates high enough to have air speeds higher than the threshold values, where the extraction rate is dependent mainly on diffusion of the analyte through the adsorbent pores or through the liquid coating film (Koziel et al., 2000).
For the device shown in Figure 4 this was achieved by using a modified DC-powered hair dryer. The reversion of the direction of the air flow was made to avoid the contact of the fiber with potential artifacts originated from the dryer body and motor.

Quantitative Analysis of VOCs in Indoor Air.

Table 2 compares concentrations of several aromatic VOCs found with the PDAS-SPME sampling (non-equilibrium diffusion-based quantification) and concentrations obtained with simultaneous application of NIOSH #1501 standard method. For PDAS-SPME calculations, the values for the needed constants were: \( b = 0.0120 \text{ cm} \); \( L = 1 \text{ cm} \) (both previously measured in the laboratory); \( M_{\text{air}} = 28.97 \text{ g/Mol} \); \( V_{\text{air}} = 20.1 \text{ mL} \) and \( \nu = 0.15 \text{ cm}^2/\text{s} \). The sampling time and air flow rate for NIOSH analysis was adjusted according to the expected concentrations of contaminants in each sample, based on preliminary exploratory extractions: 91 min for the Vehicle Shop air and 215 min for the Mechanical Shop air, with a flow rate of 138 mL/min (sampled air volumes: 12.6 L for Vehicle Shop and 29.7 L for Mechanical Shop). Under these conditions, no analyte breakthrough was observed when applying the NIOSH method. It should be emphasized that the sampling time for the NIOSH-based sampling was a few orders of magnitude greater than the sampling time associated with PDAS-SPME. However, none of the existing standard methods could be compared with 30 s PDAS-SPME sampling time.

Table 2. Concentrations in ppb v/v of aromatic VOCs in indoor air measured by PDAS-SPME and NIOSH standard Method #1501.

<table>
<thead>
<tr>
<th></th>
<th>Vehicle Shop</th>
<th></th>
<th>Mechanical Shop</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPME</td>
<td>NIOSH</td>
<td>SPME</td>
<td>NIOSH</td>
</tr>
<tr>
<td>Benzene</td>
<td>48 ± 10 (^{a})</td>
<td>- (^{b})</td>
<td>17 ± 4</td>
<td>-</td>
</tr>
<tr>
<td>Toluene</td>
<td>212 ± 43</td>
<td>215</td>
<td>62 ± 9</td>
<td>73</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>60 ± 8</td>
<td>48</td>
<td>n.d. (^{c})</td>
<td>n.d.</td>
</tr>
<tr>
<td>(p)-xylene</td>
<td>189 ± 43</td>
<td>222</td>
<td>25 ± 5</td>
<td>n.d.</td>
</tr>
<tr>
<td>(o)-xylene</td>
<td>249 ± 35</td>
<td>137</td>
<td>18 ± 5</td>
<td>n.d.</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>202 ± 28</td>
<td>75</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Uncertainties expressed as estimates of standard deviation of triplicates. \(^{a}\) = not quantifiable (see text), \(^{b}\) = not detected.

The PDAS-SPME results obtained for the Vehicle and Mechanical Shops were similar to those from NIOSH analysis, except for the hydrocarbons with higher molecular weight in the set (\(o\)-xylene and mesitylene), which are underestimated by the NIOSH method. A possible cause for this could be associated with the incomplete desorption of these analytes from the charcoal tubes employed in the NIOSH method, when using the recommended desorption procedure. Another reason for the observed discrepancies in measured concentrations could be due to the widely different sampling times used in both methods. The NIOSH-based concentration can be considered as a time-weighted average sample over a long sampling period. In contrast, the PDAS-SPME concentrations can be associated with spot or grab 30 s sampling. In addition, it was not possible to measure benzene concentration in the evaluated samples using this method. Benzene is a common and significant contaminant in the \(\text{CS}_2\) solvent recommended for the desorption step in the NIOSH method.
VOC concentration levels can be considered typical of indoor air in occupational environments. Expressed as estimates of relative standard deviations ($s_R$), the precision of PDAS-SPME results ranged from 13% to 28%, with an average value of 20%. These results can be compared to those presented in an extensive study of NIOSH charcoal tube collection methods for airborne organics (NIOSH, 1994). The $s_R$ values calculated from the data presented in this study ranged from 0.4% to as much as 69%, with an average of 15% (for xylene $s_R$ ranged from 5.2% to 22%, with an average of 10% and for benzene, from 4.3% to as much as 43%, with an 15% average). Therefore, precision for the PDAS-SPME method can be considered in the same order of magnitude (if not better for some analytes) to the range of precision reported for NIOSH standard method.

An estimate of the detection limits of PDAS-SPME was provided by the lab air samples analysis. For sampling close to the solvent bin (18 ± 6) ppbv benzene, (6 ± 3) ppbv of toluene, and (2 ± 1) ppbv of xylene were detected, and for the air in the instrument room (3 ± 1) ppbv of toluene and (2 ± 1) ppbv of xylene; other analytes were not detected. Those results show that the detection limits for PDAS-SPME are in the low ppbv range. Comparison with NIOSH method was not considered valid here, since for the same samples no aromatic hydrocarbons were detected with this method even extending the sampling volumes to values up to 50 L, except for toluene in one of the samples. For the sampling volumes employed in the Vehicle and Mechanical Shops analysis, the detection limits calculated according to data provided in Method #1501 would be in the range between 6 and 100 ppbv for Mechanical Shop air sampling and 15 to 230 ppbv for Vehicle Shop air sampling, depending on the analyte in consideration. Therefore, PDAS-SPME can be considered as more sensitive than the standard NIOSH #1501 method.

The assessment of long-term concentrations in air could be also accomplished using this methodology. This would require averaging several measurements made during a longer period of time. For these cases, procedures such as standard NIOSH methods or similar alternatives would be more adequate. Since the sampling time is one of the variables needed to calculate the concentration, errors in its measurement would reflect in the accuracy and precision of results. Such errors could be significant considering that these short exposure times should be manually measured. Another possible limitation of the rapid sampling method is the dependence of the results on dimensional parameters of the fibers (their radius and length, which are constants in the model’s equations). Fibers should be checked in respect to their true dimensions to ensure accurate measurements, as well as the integrity of the coating.

**Conclusion**

This work demonstrated that the combination of SPME and the simple and inexpensive (ca. US$10) PDAS-SPME device was a powerful tool for quantitative analysis of VOCs in occupational air (Augusto et al., 2001). When compared to SPME extraction with simple “static” exposure of the fiber to the air, the application of PDAS-SPME increased significantly the number of detectable analytes, the adsorbed amounts, and the method sensitivities. Findings in this work suggest that PDAS-SPME can provide more accurate qualitative profiles of extremely diluted samples such as natural aromas and odors (data not shown). Experiments are currently conducted to apply the rapid SPME sampling method to determination of chemical composition and concentrations of agricultural odors.

The use of PDAS-SPME also allowed the application of non-equilibrium diffusion-based quantification to air samples using fibers coated with solid (porous) polymers. The use of short sampling time minimized the effects of inter-analyte displacement that in the past prevented the use of these fibers for accurate quantitative air analysis. Also, this non-equilibrium model can
result in quantitative analysis without need of a calibration curves, provided that some constants, e.g., analyte diffusion coefficient in air and the detector response factor, are known. When compared to standard methodologies, a 30 s sampling using PDAS-SPME allowed measurement of VOC concentrations that where not detected by NIOSH standard method, even after several hours of extraction using expensive (air sampling pumps) and non-reusable (charcoal tubes) materials.

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