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Time-weighted average sampling of volatile and semi-volatile airborne organic compounds by the solid-phase microextraction device

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Abstract

The ultimate goal of the chemist is to perform sample preparation, and analysis, if possible at the place where a sample is located rather than moving the sample to laboratory, as is common practice in many cases at the present time. This approach eliminates errors and time associated with sample transport and storage and therefore it would result in more accurate, precise and faster analytical data. In addition to portability, two other important features of ideal field sample preparation technique are elimination of solvent use and integration with a sampling step. A method is developed which addresses these requirements for the determination of time-weighted average concentration of gas phase compounds using a solid-phase microextraction device. Quantification of target analytes in air using this method can be carried out without external calibration. The volatile and semi-volatile organic compounds in air diffuse into the fiber coating which is retracted a known distance into its needle housing during the sampling period. The coatings used are poly(dimethylsiloxane) and poly(dimethylsiloxane)-divinylbenzene. The sampling rate at which gas phase analytes load onto the fiber is determined for a wide range of hydrocarbons. There is a good agreement between the theoretical and experimental sampling rates. Sampling time ranges from 1 min to 24 h depending on the coating used and its retraction distance. Effect of the flow-rate on the uptake rate by the fiber is studied. The method is tested in the field and compared with National Institute of Occupational Health and Safety Method 1550. Good agreement between the results is obtained. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrocarbons make up a major class of air pollutants [1]. They play a very important role in tropospheric chemistry especially in promoting photochemical smog formation [2,3].

Airborne organic compounds are classified into non-volatile, semi-volatile and volatile categories.

Semi-volatile compounds are classified by Lewis [4] as compounds with vapor pressure (V_p) between 10^{-1} and 10^{-7} Torr (1 Torr=133.322 Pa) at 25°C. Volatility of hydrocarbons decreases with increasing molecular mass. This might indicate that only the lighter ones (C_1 to C_4) contribute significantly to air pollution. It is true that the concentration of the volatile hydrocarbons exceeds the concentration of the less volatile compounds, but the latter compounds pose a danger as respiratory and general environmental contaminants [5]. Volatile organic compounds (VOCs) are normally present in air at levels above 0.1 $\mu\text{g}/\text{l}$, while semi-volatile organic

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compounds (SVOCs) are normally present at the ng to pg/l range [4].

The US Occupational Safety and Health Administration (OSHA) has developed standards to protect employees against harmful chemicals. These standards are termed permissible exposure limits (PELs). The primary mechanism for calculating exposure limits is the 8-h time-weighted average (TWA) sampling. The PEL-TWAs refer to airborne concentrations to which nearly all workers may be exposed for 8 h per day, 40 h per week, for a working lifetime without adverse effects.

There are two approaches for collecting integrated or TWA samples [6]. The first is by taking a large number of grab samples during the time period of interest and averaging the concentrations obtained (Eq. (1)):

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

where C_1 is the analyte concentration for time t_1 , C_2 is the analyte concentration for time t_2 , etc. We would need 48 samples to obtain the TWA concentration of a compound over an 8-h period if a 10-min grab sampling time were used. Sometimes 5-min sampling intervals are needed for a more accurate description of the average concentration. Therefore obtaining a TWA concentration using this approach is impractical and expensive. The second way is achieved by collecting one sample over the time period of interest. Using this approach a TWA concentration is obtained by acquiring one sample with one sampler. The analytes are mass loaded in direct proportion to their concentration in air at given time. This approach is highly recommended due to its simplicity and cost effectiveness because a lower number of samples are acquired [7].

Loading of an air sample can be carried out with either active sampling or diffusive (passive) sampling. The first approach utilizes pumps to draw air at a constant flow-rate through a bed of solid sorbents, liquid absorbents or into other appropriate collection devices [8,9]. The second approach relies on diffusion to move the analytes of interest to the sampling media [10]. Diffusive sampling has been used since 1973 for monitoring air pollutants [11]. This approach is becoming increasingly popular due

to the fact that air sampling pumps are usually expensive, noisy, and their potentially faulty batteries make them unreliable [12].

Solid-phase microextraction (SPME) is shown in this paper to be a viable alternative to TWA sampling of hydrocarbons with low to high vapor pressure. Air sampling with SPME provides significant advantages over traditional methods. It offers solvent-free operation, convenient coupling with field analytical instruments, good accuracy, precision, cost effectiveness and the simplicity of operation and calibration. SPME has been successfully used for spot sampling organic compounds in gaseous, liquid and solid matrices [13,14]. The portability of its device makes SPME the ideal sample preparation technique for field analysis.

This paper discusses the use of SPME device as a TWA sampler for a standard gas mixture of airborne hydrocarbons. An SPME device can be used as a TWA diffusive sampler by simply retracting the coated fiber a known distance into its needle housing during the sampling period. Fig. 1 shows the in-tube SPME fiber coating retracted a distance, Z , relative to the needle opening. A is the needle opening surface area.

2. Theory

During the process of diffusion, a linear concentration profile exists across Z as shown in Fig. 2. By using Fick's law of diffusion, it is possible to determine the amount of analyte loaded on the fiber coating, dn , during the sampling time, dt [14]:

$$dn = -AD_g \cdot \frac{dc}{dx} \cdot dt = -AD_g \cdot \frac{\Delta C(t)}{Z} \cdot dt \quad (2)$$

where $\Delta C(t)/Z$ is the concentration gradient value along Z , the distance from the needle opening to the sorbent surface; D_g is the diffusion coefficient of the analyte in the gaseous phase. $\Delta C(t) = C_z - C(t)$ where C_z is the gas-phase analyte concentration at the coating position and $C(t)$ is a time dependent concentration of the analyte at the needle opening. $C_z = 0$ if the sorbent has a high capacity, i.e., acts as zero sink. A zero sink sorbent means that the mass loading rate is not affected by the amount of analyte already sorbed.

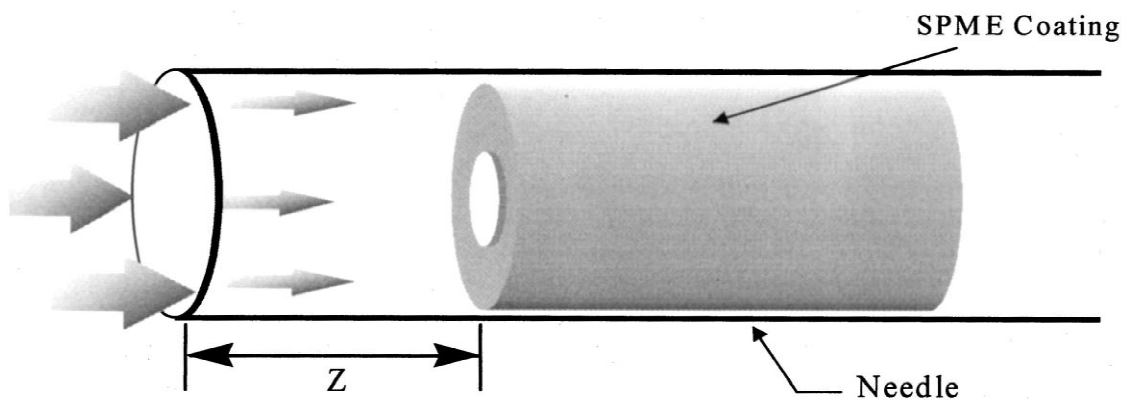


Fig. 1. SPME device in the retracted mode for TWA sampling.

After integration of both sides over time Eq. (2) reduces to

$$n = D_g \cdot \frac{A}{Z} \int C(t) dt \quad (3)$$

Eq. (3) is valid only when the amount of analyte sorbed by the fiber coating is a small fraction of the

equilibrium amount (typically less than 5%) to meet the assumption: $C_z = 0$.

The product of D_g and A divided by Z for a certain analyte and SPME device needle defines sampling rate SR and it is a constant at a given temperature.

$$SR = D_g \left(\frac{A}{Z} \right) \quad (4)$$

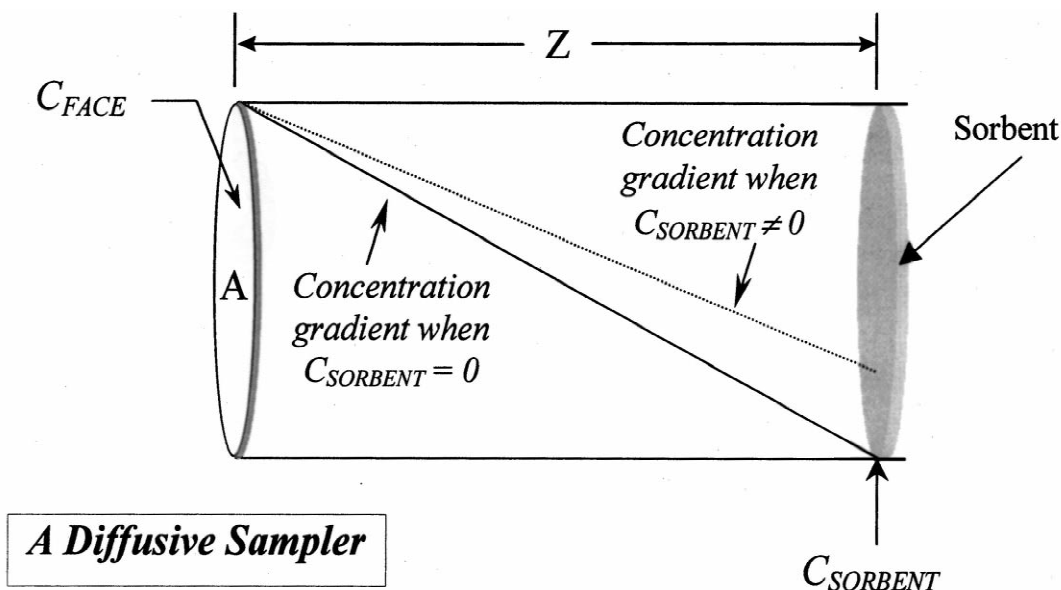


Fig. 2. The concentration gradient of an analyte produced between the opening of the needle and of the position of the sorbent coating. Z is the path length and A is the surface area of the opening.

Rewriting Eq. (3) using Eq. (4)

$$n = \text{SR} \int C(t) dt \quad (5)$$

For a constant analyte concentration in gas, Eq. (4) reduces to Eq. (6). Therefore the K' value for each analyte can be determined empirically using Eq. (6):

$$\text{SR} = \frac{n}{Ct} \quad (6)$$

SR can be determined experimentally using the above equation by determining the mass uptake rate of a certain compound by SPME fiber coating retracted to a known distance at a certain concentration. Once K' is determined for an analyte with the SPME fiber, it can be used to quantify unknown concentrations by simply knowing the amount of analyte, n , sorbed over a certain time, t .

Eq. (3) indicates that the amount of analyte sorbed is proportional to the diffusion coefficients of analytes in the gaseous phase, D_g , area of the needle opening, A , and inversely proportional to the distance Z . Therefore the amount of analytes sorbed on the fiber coating can be decreased by simply increasing Z (Fig. 1). This will accommodate higher concentrations or longer sampling times. If SR was determined at Z and a sample is acquired at Z' then the new SR value is simply calculated using Eq. (7).

$$\text{SR}_{(Z')} = \text{SR}_{(Z)} \cdot \frac{Z'}{Z} \quad (7)$$

Similar correction can be performed for different temperatures considering that only the diffusion coefficient is affected by this parameter. Unlike conventional grab sampling by SPME, TWA by the SPME device using this approach is used far from equilibrium conditions [15].

3. Experimental

3.1. Chemicals

C_5 – C_{15} n -alkanes were purchased from Sigma–Aldrich (Mississauga, Canada). Carbon disulfide was from BDH (Toronto, Canada). All chemicals were

used as purchased after checking for impurities by GC injection.

3.2. Materials

The carrier gas was helium. Nitrogen and hydrogen gases were used for flame ionization detection (FID). All gases used were ultra high purity (UHP) grade and purchased from Praxair (Waterloo, Canada). Air for the FID and gas generator was generated by a zero air generator (Model 76-103) purchased from Whatman (Haverhill, MA, USA). The Razel (A99) syringe pump used to deliver the analyte mixture for standard gas generator was purchased from Razel Scientific Instruments (Stamford, CT, USA). Swagelok metering valves, 1/8 and 1/16 in. (1 in. = 2.54 cm), adapters, and tees were purchased from Weston Valves and Fittings (Mississauga, Canada). SPME fibers [100 μm poly(dimethylsiloxane) (PDMS) and 60 μm PDMS–divinylbenzene (DVB)], syringes and charcoal tubes were from Supelco (Mississauga, Canada). All retracted fiber path lengths (Z) and surface areas (A) were measured by inserting a steel tube that had an outer diameter equal to the needle tube inner diameter, then measuring the depth and outer diameter of the inserted tube. Mechanical air pumps were purchased from A.P. Buck (Orlando, FL, USA). Air flow-rates into the mixing chamber were controlled using Sidetrack mass flow controllers purchased from Sierra Instruments (San Jose, CA, USA). Actual air flow-rate was verified using primary gas flow standard, mini-Buck calibrator purchased from A.P. Buck. Air temperature settings are maintained at $25 \pm 0.5^\circ\text{C}$ by an Omega heating tape and heat control device and the chamber was surrounded by Ottawa sand purchased from Fisher Scientific (Nepean, Canada) for heat insulation (as shown in Fig. 3). All chamber temperatures were measured inside the chamber with a NIST (National Institute of Standards and Technology) calibrated thermocouple.

3.3. Instrumentation

All analyses were performed on a Varian GC 3400 gas chromatograph (Varian Associates, Sunnyvale, CA, USA) equipped with a 30 m \times 0.25 mm, 1 μm DB-5 column (J&W Scientific), a septum-equipped

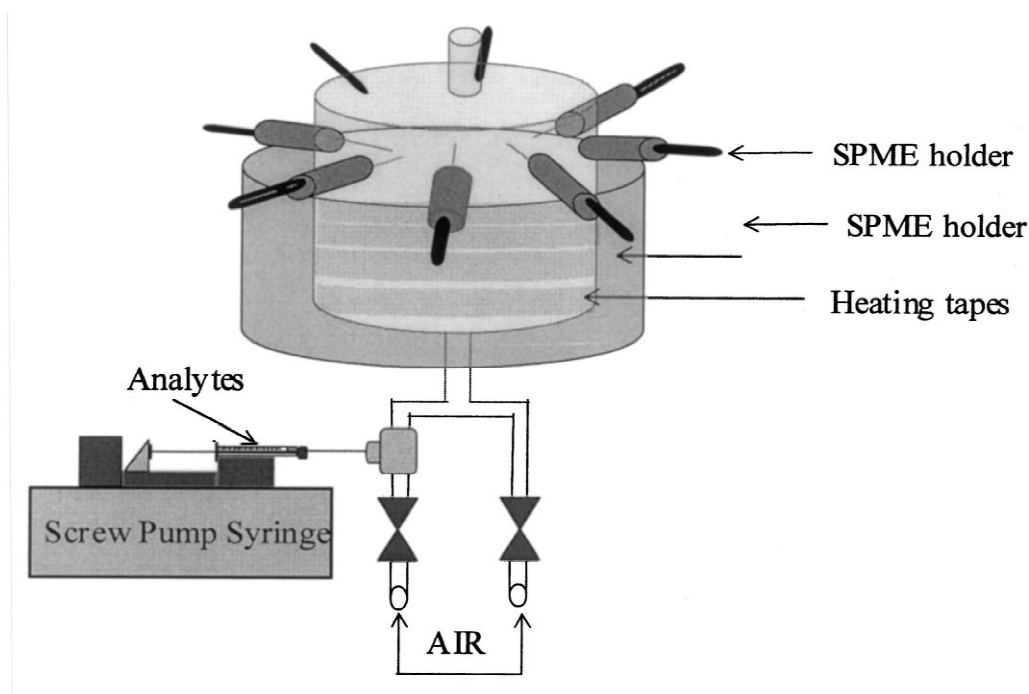


Fig. 3. Schematic representation of the standard gas generating device.

programmable injector (SPI) with SPME insert, and a FID system. The carrier gas was helium (20 p.s.i. head pressure; 1 p.s.i.=6894.76 Pa). The column temperature program used was: initial 45°C for 1 min, 15°C/min to 230°C, hold for 5 min. Detector response factors were determined by syringe injection of a standard solution of the hydrocarbons in carbon disulfide, using the following column temperature program: 45°C for 1 min, 15°C/min to 230°C, hold for 5 min. In this experiment, the SPI was temperature programmed (45°C for 0.15 min, 300°C/min to 250°C, hold for 1 min; liquid CO₂ was used to cool the injector between injections).

3.4. Standard gas generating device

A standard gas generating device was constructed as shown in Fig. 3. All copper and stainless steel tubing connecting the compressed air to the standard gas generating device was thoroughly cleaned with solvent, allowed to dry, then flamed. The 1.5-l chamber was made from clear glass with nine sampling ports plugged with half hole type Thermogreen LB-1 septa, to allow multiple sampling ports.

Air temperature settings were maintained at 25±0.5°C by an Omega heating tape and heat control device and the chamber was surrounded by Ottawa sand purchased from Fisher Scientific for heat insulation. All chamber temperatures were measured inside the chamber with an NIST calibrated thermocouple. The concentrations of C₅–C₁₅ *n*-alkanes in air from the standard gas generating device were verified by following the National Institute for Occupational Safety and Health (NIOSH) Method 1550 for the determination of airborne hydrocarbons.

Eq. (8) shows how the theoretical analyte concentrations in the chamber were determined.

$$C_g (\mu\text{g}/\text{l}) = \left[\frac{(\mu\text{g}/\text{min})_{\text{mix}}}{(\text{l}/\text{min})_{\text{air}}} \cdot \frac{\text{Mass of analyte}}{\text{Total mass of mixture}} \right] \quad (8)$$

Concentration can be converted to parts per million by volume (ppmv) using Eq. (9) with the molar gas volume at the specified temperature and pressure as well as the analyte molecular mass.

$$C_{g \text{ (ppmv)}} \left(\frac{\mu\text{l}}{\text{l}} \right) = C_{g \text{ (}\mu\text{g/l)}} \cdot \left(\frac{0.0821 \text{ l atm mol}^{-1} \text{ K}^{-1} \cdot 298 \text{ K}}{1 \text{ atm} \cdot M_r \text{ g mol}^{-1}} \right) \quad (9)$$

3.5. Preparation of analyte mixture

Appropriate amounts of C_5 – C_{15} *n*-alkanes were spiked with a gas-tight syringe through a PTFE-lined septum starting with the least volatile to a clean preweighed vial and weighed again after spiking each compound. Standard amounts added were 0.84 mg of pentadecane, 1.46 mg of tetradecane, 2.95 mg of tridecane, 5.93 mg of dodecane, 1.17 mg of undecane, 2.28 mg of decane, 4.61 mg of nonane, 9.62 mg of octane, 1.75 g of heptane, 4.35 g of hexane and 6.43 g of pentane. Smaller amounts of the less volatile compounds were added due to the fact that they usually exist in air at lower concentrations. After preparation, the vial including the mixture was manually agitated and dispensed into clean 2-ml vials equipped with PTFE-lined septa, where no headspace was left in the vial. A 1-ml Hamilton gas-tight syringe was filled with the mixture and placed in the syringe pump, to deliver the analyte mixture at $42 \mu\text{g}_{\text{mix}}/\text{min}$. The syringe pump was calibrated for analyte delivery to $42 \mu\text{g}/\text{min}$ of the analyte mixture into the mixing tee of the standard mixture. Calibration was carried out in three different ways. In the first approach the preweighed syringe was left to deliver the mixture for a specific period of time and then weighed again after delivery. In the second, the volume difference was obtained by recording the liquid level before and after delivery. In the third the analyte mixture was delivered into a pre-weighed tightly capped PTFE vial, which was then weighed after a specific period of time. The difference between the three methods was less than 1%. Time periods for testing ranged from 1 h to 4 days.

Concentration in the chamber was changed by simply changing the air flow-rate, or by preparing a different standard mixture with different liquid concentration.

For calibration curves, $10 \mu\text{l}$ of each hydrocarbon was added to 1 ml of carbon disulfide and then serially diluted by 1:10 ratio. Four dilutions were performed, to produce an overall $10\,000\times$ dilution.

The chamber was allowed to reach steady state after each change or alteration in gas concentration. The inlet air flow-rate was set at 300 ml/min and it was verified by a primary gas flow standard calibrator.

4. Results and discussion

4.1. Integrated sampling with the 100 μm PDMS fiber

The 100 μm PDMS fiber was used in experiments to determine the mass uptake rate. SR values were determined from Eqs. (4) and (6) for different *Z* values of 0.3, 1 and 3 cm. Figs. 4 and 5 show representative mass loading rates for some of the *n*-alkanes with the 100 μm PDMS fiber. The intercept value for the linear uptake rate represents the amount adsorbed on the stainless steel tubing. The higher the molecular mass of the compound, the higher the intercept value. As we see from Figs. 4 and 5, the intercept value increases significantly as we go from pentane to tetradecane. However, for a specific analyte, this value is proportional to the concentration of the gas analyte and the pathlength *Z*. Therefore if these SR values are used to determine an unknown concentration, a positive error will be introduced, which is the intercept value. This error becomes more significant as the volatility of the compound decreases. The use of deactivated stainless steel tubing should reduce the intercept value and minimize this error.

The mass loading rates and linearity for each analyte are summarized in Table 1. Table 2 shows the comparison between the theoretical SR values calculated from first principles (using Eq. (4)) and experimental values (using Eq. (6)) for *Z* values of 0.3, 1, 3 cm.

Mass loading rates for the least volatile compounds like tetradecane and pentadecane were not determined accurately. Uptake rates calculated experimentally were higher than the expected theoretical values due to the adsorption of these compounds on the stainless steel needle. This can be reduced by using deactivated surface tubing. However, experimental values for the most volatile compounds like pentane and hexane were less than expected

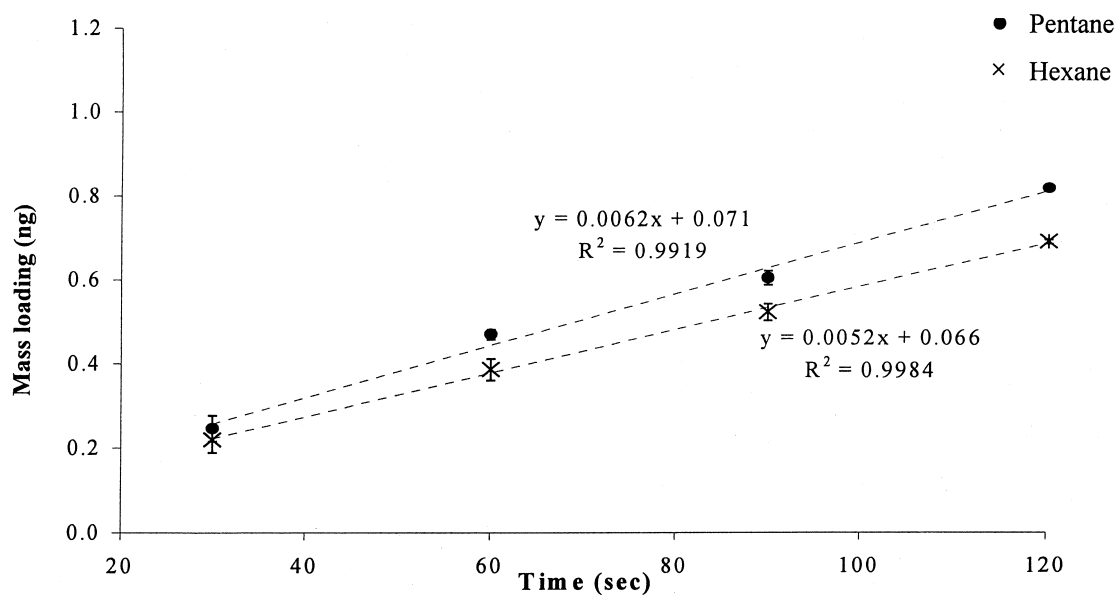


Fig. 4. Uptake rate for pentane and hexane by the 100 μm PDMS fiber ($Z=0.3$ cm).

from the theory. These compounds have high vapor pressure and diffusion coefficients which force a fraction of them to leave the fiber coating before desorption in the GC system. In addition, due to their

low partition coefficient, these compounds reach equilibrium in a short time which makes it difficult to load less than 5% of the equilibrium amount. These problems were solved by using a strongly

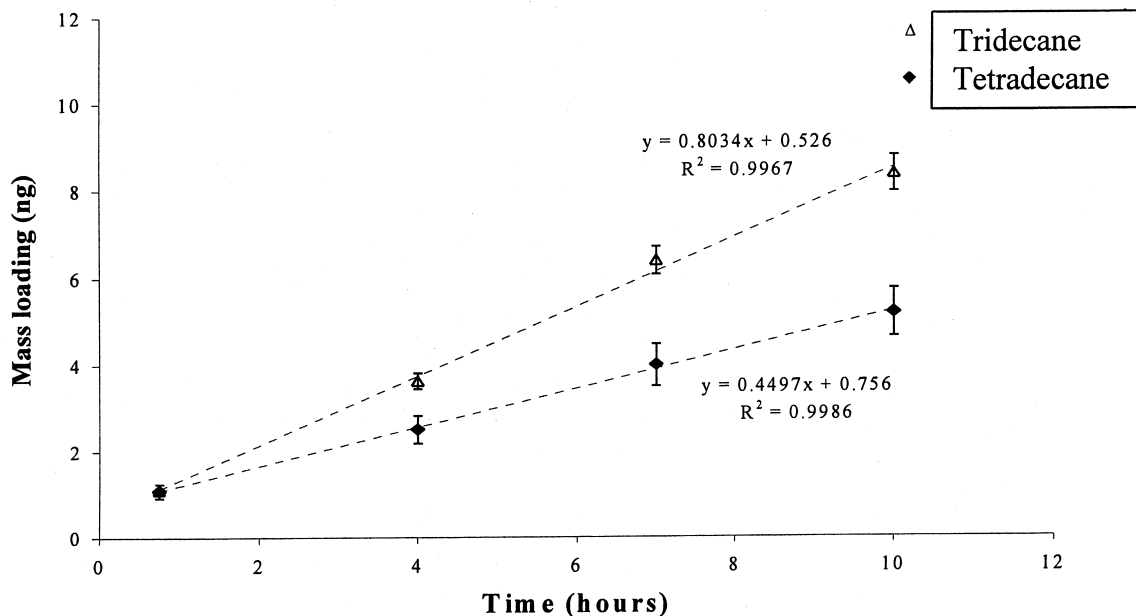


Fig. 5. Uptake rate for tridecane and tetradecane by the 100 μm PDMS fiber ($Z=0.3$ cm).

Table 1
Mass loading rate for C₅–C₁₅ *n*-alkanes by the 100 μm PDMS fiber (A=0.00086 cm²)

Analyte	Concentration (ng/ml)	Uptake rate (ng/min)	R ²	D _g (cm ² /s)	SR (1) ^a (ml/min)	SR (2) ^a (ml/min)
Pentane	56.5	330.0	0.9922	0.092	0.0071	0.016
Hexane	43.7	312.0	0.9984	0.084	0.0081	0.014
Heptane	12.37	126.3	0.9984	0.078	0.010	0.013
Octane	6.40	64.8	0.997	0.073	0.010	0.013
Nonane	6.50	63.7	0.9889	0.069	0.0098	0.012
Decane	3.02	32.5	1	0.066	0.011	0.011
Undecane	3.36	34.3	0.9995	0.0630	0.010	0.011
Dodecane	1.38	13.7	0.9993	0.060	0.010	0.010
Tridecane	1.38	13.4	0.9967	0.058	0.0097	0.0099
Tetradecane	0.69	7.5	0.9986	0.056	0.011	0.0096
Pentadecane	0.69	8.4	0.9175	0.054	0.012	0.0092

^a SR: First-order rate constant for the analyte uptake when the fiber was retracted 0.3 cm, (1) experimental, calculated using Eq. (6), (2) theoretical, calculated using Eq. (4).

sorptive coatings like the PDMS-DVB as will be discussed later.

Figs. 6 and 7 show another comparison between theoretical and experimental values for SR when the fiber was retracted 0.3 and 3 cm, respectively. Both experimental and theoretical values of SR were divided by the diffusion coefficient and plotted versus the carbon number of each compound. According to Eq. (3) the theoretical factor SR/D_g is a constant number for a certain SPME device and fiber retracted to a known distance no matter what the compound is.

The experimental SR values for the most volatile compounds fell below the theoretical values as shown in Fig. 6 due to the loss of these compounds from the fiber coating prior to desorption. However, higher SR values for the least volatile compounds are due to the adsorption of these compounds on the stainless steel tubing of the needle. The problem of adsorption of the least volatile compounds on the stainless steel tubing is aggravated by retracting the fiber further into its housing needle (3 cm) as shown in Fig. 7. The area of the adsorptive surface increases as we retract the fiber further into the needle.

Table 2
Comparison between experimental and theoretical K' values for different pathlengths Z

Analyte	SR values (ml/min)					
	Z=0.3 cm		Z=1 cm		Z=3 cm	
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
Pentane	0.016	0.0071	0.0047	0.0035	1.57	0.86
Hexane	0.014	0.0081	0.0043	0.0036	1.44	1.24
Heptane	0.013	0.010	0.0040	0.0037	1.33	1.24
Octane	0.013	0.010	0.0038	0.0036	1.25	1.18
Nonane	0.012	0.0098	0.0035	0.0037	1.18	1.21
Decane	0.011	0.0108	0.0034	0.0031	1.13	0.96
Undecane	0.011	0.010	0.0032	0.0028	1.08	1.11
Dodecane	0.010	0.010	0.00308	0.0028	1.03	1.08
Tridecane	0.0099	0.0097	0.0030	0.0027	0.99	1.31
Tetradecane	0.0096	0.0108	0.0029	0.0028	0.96	2.09
Pentadecane	0.0092	0.0122	0.0028	0.0039	0.92	4.21

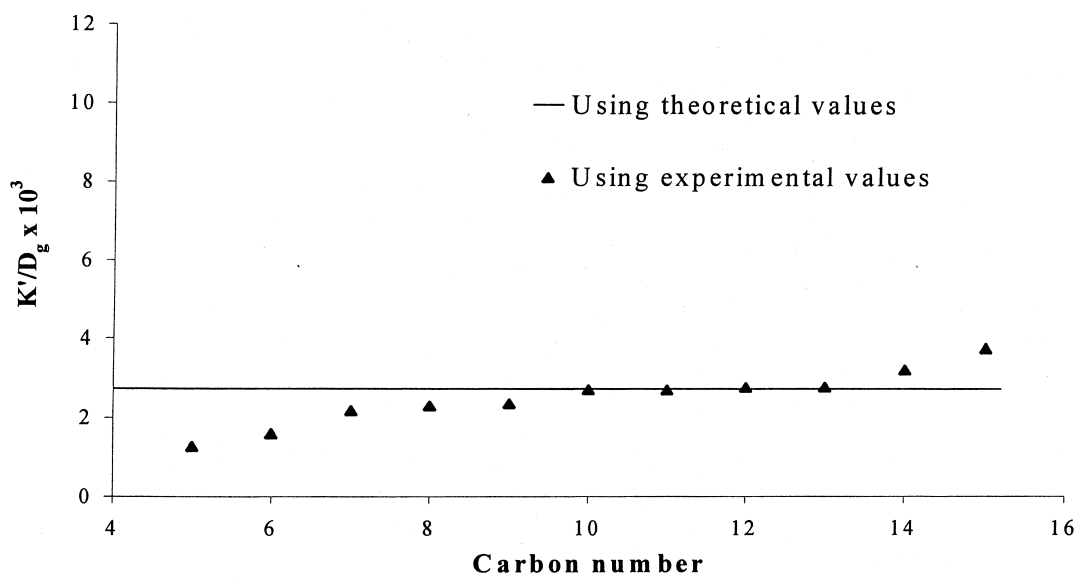


Fig. 6. A plot of SR/D_g , using experimental and theoretical SR ($Z=0.3$ cm), versus the carbon number of each analyte for 100 μm PDMS fiber.

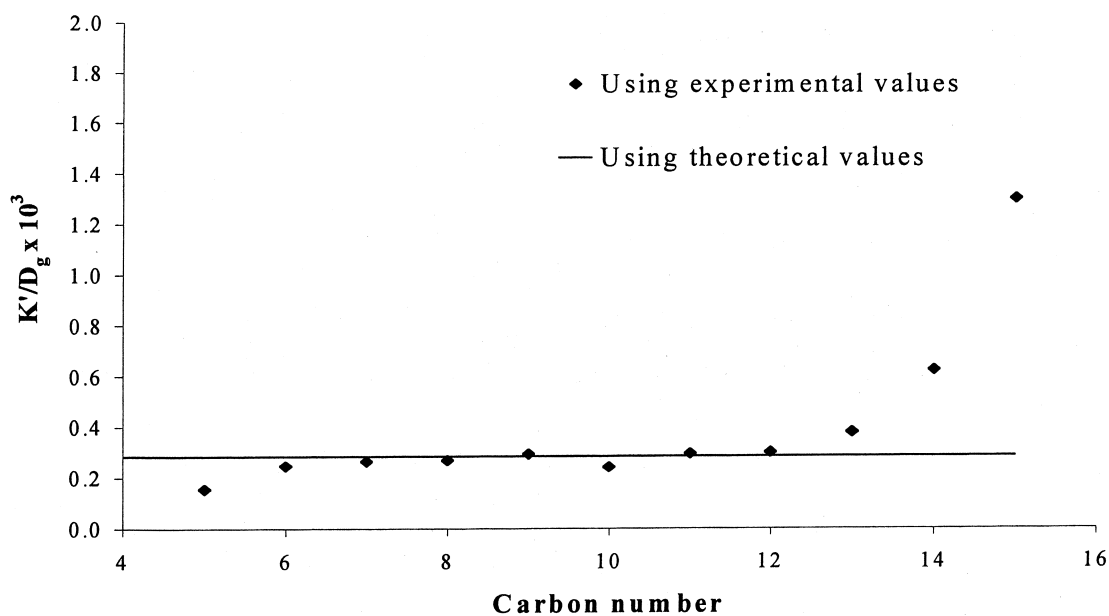


Fig. 7. A plot of SR/D_g , using experimental and theoretical SR ($Z=3$ cm), versus the carbon number of each analyte for the 100 μm PDMS fiber.

Table 3

Comparison between experimental and theoretical first-order uptake values (SR) by SPME with 60 μm PDMS-DVB (retracted 0.3 cm) SR (1) and SR (2) are defined in Table 1

Compound	Pentane	Hexane	Heptane	Octane	Nonane	Decane	Undecane	Dodecane
SR (1)	0.014	0.013	0.011	0.0093	0.0083	0.0092	0.0081	0.0095
SR (2)	0.016	0.014	0.013	0.012	0.012	0.011	0.011	0.010

However, retracting the fiber further slows the extraction process and minimizes the loss of the most volatile compounds.

The results shown above demonstrate a good agreement between the experimental results and theoretical predictions. The uptake rate by the coating is totally depending on the diffusion coefficient of the analyte when Z is kept constant.

4.2. Integrated sampling with the 60 μm PDMS-DVB fiber

The purpose of using the PDMS-DVB coating was to minimize the loss of volatile compounds from the fiber coating. The same standard gas mixture was

used for this study, however, only the more volatile compounds C_5 – C_{12} were studied. Table 3 shows a comparison between the experimental and theoretical SR values obtained by using SPME with PDMS-DVB coating retracted 0.3 cm.

The results obtained demonstrated that PDMS-DVB fiber can be used successfully for the TWA sampling of volatile compounds. Fig. 8 shows another comparison between the experimental and theoretical values by plotting SR/D_g versus carbon number. The PDMS-DVB coating cracks when exposed to high temperatures as 250°C. Desorption time used was 2 min, which is not long enough to desorb quantitatively the least volatile compounds and therefore they were not included in the studies.

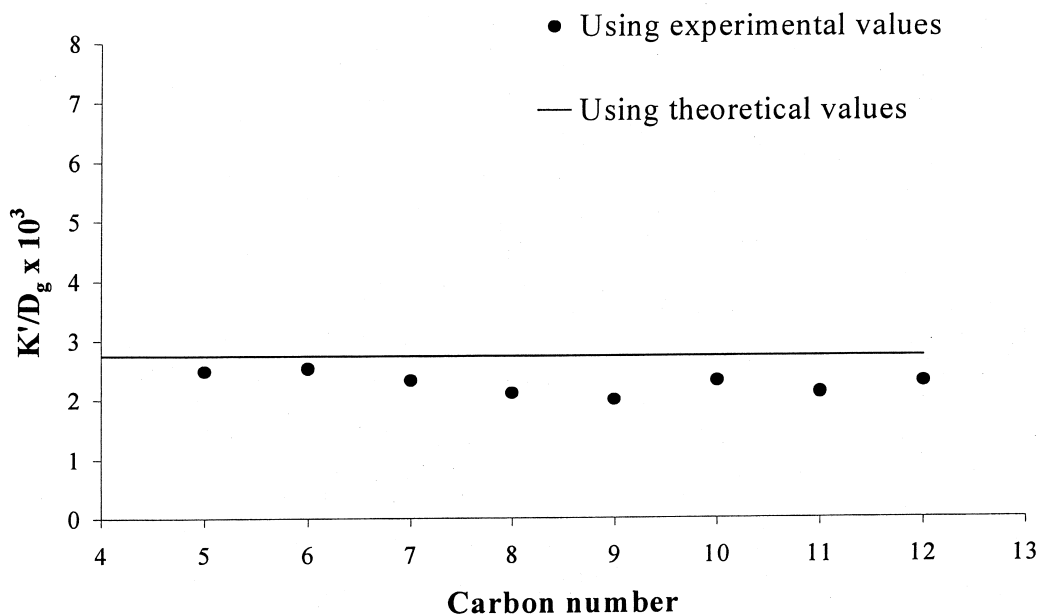


Fig. 8. A plot of SR/D_g , using experimental and theoretical SR ($Z=0.3$ cm) versus the carbon number of each analyte for the 60 μm PDMS-DVB fiber.

The SR values for the less volatile compounds obtained using the PDMS-DVB coating fell below the theoretical values.

4.3. Effect of the flow-rate on the uptake rate by the SPME device

The inlet flow-rate was set at 300 ml/min for all the experiments discussed earlier. The effect of the flow-rate on the determination of SR was studied by repeating the previous experiments at different flow-rates: 200 and 250 ml/min. The 100 μm PDMS fiber was used. For a 250 ml/min flow-rate, the standard liquid mixture in the syringe was diluted 1.2 times by adding appropriate amount of pentane to keep the same concentration in the standard gas generator as in Table 1. For 200 ml/min flow-rate, it was diluted 1.5 times. See Eq. (8). Therefore the concentration of pentane was different for each flow-rate studied and the concentration of each of the $\text{C}_6\text{--C}_{15}$ *n*-alkanes was kept constant in the gas chamber.

Table 4 shows the SR values at inlet air flow-rates of 200 and 250 ml/min compared to the SR determined at 300 ml/min inlet air flow-rate.

Table 4 shows that there is no effect of the flow-rate on the uptake rate by the SPME fiber. This indicates that TWA sampling by the SPME device is dependent only on the diffusion coefficient of the compound into the SPME fiber. Since the concentration of pentane was different, we can say that there is no effect of concentration on the SR value

Table 4
Comparison between SR values determined at different inlet air by the 100 μm PDMS fiber (retracted 0.3 cm)

Compound	SR		
	300 ml/min	250 ml/min	200 ml/min
Pentane	0.0071	0.0078	0.0076
Hexane	0.0081	0.0070	0.0082
Heptane	0.010	0.0086	0.0097
Octane	0.010	0.0096	0.0094
Nonane	0.0098	0.0079	0.0100
Decane	0.011	0.0084	0.0085
Undecane	0.010	0.0096	0.0085
Dodecane	0.010	0.0092	0.0097
Tridecane	0.0097	0.0097	0.0092
Tetradecane	0.011	0.0099	0.0084
Pentadecane	0.012	0.011	0.011

for volatile compounds. The theoretical SR values determined by dimension of the needle, position of the fiber and the diffusion coefficient can be used to calibrate the device as long as the sorption on the needle surface is negligible.

5. Field TWA sampling by the SPME device

Indoor air was analyzed at a residential house, a residential apartment, and an old portable school. Active sampling through charcoal tubes was carried out following NIOSH Method 1550 for determination of hydrocarbons in air. A mass flow controlled air sampling pump is used to draw air through small charcoal tubes at a certain flow-rate, which was calibrated with a bubble flow meter. The analytes were then desorbed by 1 ml of carbon disulfide in PTFE capped 4-ml vial. Trip blanks were carried out for each indoor air survey.

For TWA by the SPME device, five 60 μm PDMS-DVB fibers without holders were conditioned at 250°C until clean blanks were obtained, then retracted 4 cm and capped with a PTFE cap. Three were used for sampling and the other two were used as trip blanks.

The results obtained from the field study for the determination of TWA concentration of airborne hydrocarbons using the SPME device with PDMS-DVB, and charcoal tubes are summarized in Table 5.

Eq. (6) was used for the determination of the concentration of the hydrocarbons in air using the uptake rate values SR for $\text{C}_5\text{--C}_{15}$ *n*-alkanes determined empirically with the PDMS-DVB coating (Table 3).

The major weaknesses in this air survey are the improper and incomplete identification due to the lack of GC-MS confirmation. Identification of the compounds was based on the retention time of the standard compounds. Therefore, any deviation in the retention time could yield a significant error. For the NIOSH method, the quantification was based on a single measurement. In addition, the PDMS-DVB coating cracks under the high temperature in the injector (250°C) which restricts its use to more volatile compounds that are quantitatively desorbed at lower injector temperatures. These weaknesses explain the few discrepancies between the results

Table 5

Summary of data obtained from field study using (A) TWA charcoal tubes, (B) TWA by SPME with the 60 μm PDMS-DVB fiber (retracted 0.3 cm)

Compound	Concentration ($\mu\text{g}/\text{l}$)									
	Bathroom		Kitchen		Garage		Old portable school		Grinding shop	
	A	B	A	B	A	B	A	B	A	B
Sampling time (min)	120	120	180	180	140	140	210	210	210	210
Heptane	–	–	–	–	0.72	0.59	0.067	0.084	–	–
Octane	0.070	0.094	0.23	0.78	0.46	0.54	–	–	0.019	0.032
Nonane	–	–	0.54	0.55	–	–	–	–	–	–
Decane	0.42	0.29	0.10	0.12	–	–	–	–	–	–
Undecane	0.26	0.11	0.10	0.089	–	–	–	–	–	–
Dodecane	0.058	0.17	0.10	0.13	–	–	–	–	–	–

obtained in the field using NIOSH method and the SPME device. In general, there was a good agreement between the TWA concentrations obtained in the field using the SPME device and NIOSH method.

6. Conclusion

The commercially available SPME devices can be adopted as a diffusive sampler for volatile and semi-volatile compounds. This work and Ref. [7] demonstrate that the technique provides an alternative to the much more expensive and labor intensive NIOSH methods. For improved operation the commercial SPME device should be modified for TWA sampling. Deactivated stainless steel needles should be used when sampling compounds with very low vapor pressure such as pentadecane. High capacity coatings should be used. These coatings should have high thermal stability and should be strongly bound to the silica surface to resist high temperatures required for quantitative desorption of semi-volatile analytes into injector of an analytical instrument.

The use of an SPME device with the retracted fiber mode for TWA sampling results in many advantages over traditional sampling methods. TWA sampling by SPME requires no pumps and no polluting organic solvents, which reduces significantly the sampling costs. Also, on-site rapid analysis with field portable instrumentation is possible. Properly designed device can be calibrated from first principles knowing the dimension of the needle opening, position of the fiber in the needle and the diffusion coefficient of target analyte. The gas diffu-

sion coefficient change only as a square of the molecular mass and they can be estimated from the shape of the chromatographic band for unknown compounds. Therefore by using FID the equivalence concentration value can be found even for unidentified species. Another interesting advantage of using SPME device as a TWA sampler over other available techniques is the ability to change the distance between the coating and needle opening. This makes the technique very flexible for lower and higher concentration ranges and for different sampling times. The application for air monitoring can be also extended to obtaining TWA measurement for aqueous samples.

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