

SPME-based air sampling method for inhalation exposure assessment studies: case study on perchlorethylene exposure in dry cleaning

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Abstract Exposure to perchlorethylene, especially for dry cleaning workers and for people living near dry cleaning shops, could lead to several diseases and disorders. This study examines the value of solid-phase microextraction (SPME) for sampling perchlorethylene in the atmosphere of dry cleaning shops. Carboxen/polydimethylsiloxane (CAR/PDMS) in

0.5-cm retracted mode was selected. There were no significant differences between sampling rates at different temperatures (range of 20 to 30 °C) and air velocities (2 to 50 cm/s). On the opposite, relative humidity (RH) had a significant effect on sampling rates. Method reproducibility was realized in the laboratory and field conditions and was 6.2 % and 7 to 11 %, respectively. Repeatability was also determined as 8.9 %. Comparison of the results according to the American Industrial Hygiene Association exposure assessment strategy showed the SPME sampler yields more conservative results in comparison with traditional standard method.

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Introduction

Tetrachloroethylene ($\text{Cl}_2\text{C}=\text{CCl}_2$), also known as PERC, is one of the most widely used halogenated solvents in industrial and domestic applications such as metal cleaning, dry cleaning shops, textile industries, and chemical synthesis processes. Some of its interesting features such as moderate cost, good solvent for organics, lower toxicity in comparison with other cleaning materials, and nonflammability made it a good choice in 85 % to 90 % of dry cleaning shops (Thompson and Evans 1997). US production of this compound reached 430 million pounds in 2002 (NTP

2011). According to the US Environmental Protection Agency (EPA), about 12.3 million pounds of PERC was released into the atmosphere in 1992 (US EPA 1994). Occupational and environmental inhalational exposure to PERC due to these emissions varied from subpart per billion volume (ppbv) to tens of part per million volume (ppmv). Exposure to PERC could lead to several disorders, including nervous depression, hepatocellular carcinoma, kidney and liver damages, immunotoxic and hematotoxic responses, and some renal disorders such as nephropathies (Emara et al. 2010; Lyngge et al. 2006). The International Agency for Research on Cancer (IARC) also classified PERC as a probable human carcinogen (B2) (OSHA 2005).

Inhalation exposure assessment to PERC is usually performed by active air sampling with sorbent tubes; extraction by organic solvents, especially carbon disulfide; and analysis by gas chromatography with flame ionization detector (GC–FID) (Eller and Cassinelli 1994). These methods use toxic solvents for sample extraction, which leads to the disposal of substantial volume of these solvents. These sampling trains are composed of a pump, tubing, and sorbent tube, which result in limited acceptance and applicability in occupational and environmental exposure studies.

Recent developments in solventless sample preparation techniques lead to vast applications in occupational and environmental exposure monitoring. However, much of these researches pertained to water and waste water pollutants and only a small fraction of those studies is devoted to occupational and environmental inhalational exposure monitoring. Development of environmental exposure assessment methods based on these techniques could lead to green, accurate, and affordable procedures. The ease of use and low cost of these techniques may ultimately lead to better management of atmospheric health hazards, especially in developing countries, where public health services and systems suffer from lack of trained hygienists and shortage of financial resources.

Solid-phase microextraction (SPME) is one of these techniques which was applied successfully in some occupational and environmental inhalation exposure studies (Zare Sakhvidi et al. 2011a, b). Recently, Risticvic et al. published a general protocol for the development of SPME-based sampling methods (Risticvic et al. 2010). It seems that this protocol is not completely applicable for occupational air matrices and exposure assessment studies. The steps described by Risticvic are mostly suitable

for aqueous matrices and are not applicable for gaseous matrices. In this study, we proposed a modified approach for the development of SPME-based air sampling methods for occupational exposure assessments. Use of SPME as a novel sampling device in inhalation exposure assessment has numerous benefits including no solvent consumption, less expensive procedure, and no need to train a person for sampling. There are few studies that directly examine SPME as a sampler for occupational inhalational exposures especially in its diffusive mode for prolonged sampling time. We applied this approach to the determination of inhalational exposure to PERC. The developed method was characterized, and the effects of environmental parameters and storage conditions were also studied. A comparison between the proposed SPME method and the National Institute of Occupational Safety and Health (NIOSH) 1003 method was realized on the lab and field samples. Data were also analyzed using an American Industrial Hygiene Association (AIHA) exposure assessment strategy (Bullock and Ignacio 2006).

Methods

Chemicals and materials

PERC (99.5 %), 1-butanol (99.5 %), and carbon disulfide (99 %) were obtained from Merck (Darmstadt, Germany). The low flow sampling pumps (222 series), coconut shell charcoal tubes, and soap bubble calibrator for calibration of sampling pumps were purchased from SKC Inc. (Eighty Four, PA, USA). SPME fibers, including 100 μm polydimethylsiloxane (PDMS), 65 μm PDMS/divinylbenzene (PDMS/DVB), 75 μm carboxen/PDMS (CAR/PDMS), and SPME manual holders were supplied from Supelco (Bellefonte, PA, USA). The syringe pump model Sep-10S used for generation of standard test atmospheres was purchased from Aitecs (Lithuania). The system for generation of standard atmosphere is thoroughly described in another paper (Zare Sakhvidi et al. 2012). Temperature and relative humidity (RH) in dry cleaning shop were measured by a Testo 601 hygrometer (Model Testo 601, Testoterm GmbH & Co., Germany).

Instrumentation

Analysis of all SPME samples were performed by a Varian 3800 GC–Saturn 2200 mass spectrometer (GC–MS) equipped with a capillary VOCOL column

with 60 m×0.25 mm ID, 1.5 µm film thickness (Supelco, Bellefonte, PA, USA) and helium as a carrier gas (1 ml/min). PERC was eluted at 12.4 min by the column operated at 70 °C for 1 min and then ramped at 10 °C/min to 190 °C and held for 2 min. The split/splitless injector (Varian 1177 injector) was equipped with a 0.75-mm deactivated glass liner and worked at 280 °C. The split valve was close for 3 min and then opened at a ratio of 1/20. Calibration standards for GC–MS were prepared in 1-butanol because its low vapor volume (Tuduri et al. 2001). MS calibration curve was performed by injecting 1 µl of the standard solutions into the GC–MS.

Charcoal tube samples were extracted according to NIOSH 1003(Eller and Cassinelli 1994) with 0.5 ml carbon disulfide for 30 min and were analyzed with a Unicam 4600 GC–FID (Cambridge, UK), fitted with a 1×1.5 m×4 mm ID glass column packed with 10 % PEG 20 M on Chromosorb W100-120 (Cambridge, UK). The GC–FID column was operated at 50 °C for 1 min and then ramped at 6 °C/min to 180 °C and held for 1 min. GC–FID was calibrated by standards prepared in carbon disulfide. GC calibration was checked every day by injecting a midrange standard solution. They were recalibrated if the results showed a deviation greater than 5 %. MS was also daily checked for the air/water content and ion trap count.

Air sampling

Laboratory samples were taken from dynamic and static conditions with SPME fibers in a standard-generation chamber designed by the authors (Zare Sakhvidi et al. 2012). Active sampling was performed according to NIOSH 1003 method for halogenated hydrocarbons by charcoal tubes with calibrated personal sampler pump at 150 ml/min. After sampling, the front and rear beds of the sampling tubes were extracted separately in vials by addition of 0.5 ml carbon disulfide for 30 min according to procedure described by NIOSH 1003. SPME in this study was used in the retracted mode (Koziel et al. 1999); therefore, it acts like a passive sampler and quantification can be made by Eq. 1 based on Fick's first law of diffusion (Koziel et al. 2000):

$$n = \frac{D_g \cdot A}{L} \cdot C \cdot t. \tag{1}$$

In this equation, n is the mass of analyte adsorbed on the sorbent (nanogram), t is the sampling time (min), C is the concentration (milligram per cubic meter), and D_g is the binary gas phase diffusion coefficient (square centimeter per minute) which is calculated according to the method described by Fuller et al. (1966). A is the cross-section area of the SPME needle opening (square centimeter) and measured according to procedure proposed by Koziel et al. (1999). It is equal to 0.00086 cm² for commercial SPME needles for manual injection. L is the diffusion path length (centimeter) and is preset at 0.5 cm. The term $D_g A/L$ in Eq. 1 is the theoretical sampling rate (SR_t) which is similar to pump flow rate in active sampling methods and might be calculated for passive samplers like SPME in retracted mode. SR_t for PERC in this fashion ($L=0.5$ cm as in Eq. 1, $t=25$ °C, $p=1$ atm) is 7.72×10^{-3} ml/min. Several studies showed that actual values of sampling rate (SR_a) are different in some extent with SR_t (Koziel et al. 1999; Lee and Tsai 2008). By little rearrangement, Eq. 1 can be rewritten as Eq. 2:

$$n = SR \times (C \cdot t). \tag{2}$$

Equation 2 is a general form of a simple first-order linear function. Therefore, by sampling under a specified time and concentration and plotting n against the product of C and t , SR_a can be determined as the slope of the plotted line.

Personal air samplings in the field were performed during five consecutive working days at one dry cleaning shop which used perchlorethylene as a cleaning solvent. The shop was equipped with one cleaning machine (second-generation dry-to-dry vented machine) (Earnest 2002) which is used routinely in most dry cleaning shops in Iran. Field samples were taken concurrently by the developed SPME method and the charcoal tubes based on a procedure described by NIOSH 1003 method (Eller and Cassinelli 1994). Sampling periods were varied depending on working hours of dry cleaners and were between 230 and 310 min. Temperature and air humidity of the shop were measured each day and used for selection of appropriate sampling rate for quantification of SPME samples. Qualitative analysis was made using NIST library. Quantification with MS was made in SIM mode for 166m/z.

Results

Method development steps were conducted according to Fig. 1. This process, in general, was examined

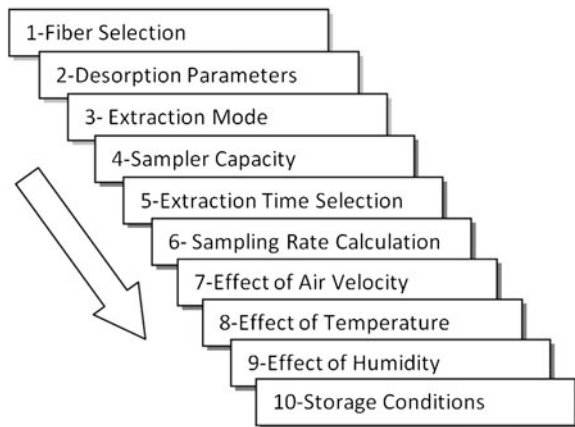


Fig. 1 A modified protocol for development of time-weighted average air sampling method with SPME

previously for development of time-weighted average (TWA) sampling method for inhalational anesthetics and epichlorhydrin by the authors (Zare Sakhvidi et al. 2011a, b, 2012). This procedure is, in some extent, similar to the general process described by Risticvic et al. (2010). However, the proposed approach in this article is optimized for development of TWA air sampling methods for inhalational exposure assessment. For example, in application of SPME as an air sampler, there is no need to consider the effect of ionic strength, pH, and water content. Therefore, we have substituted these steps with other applicable and important steps in air sampling such as environmental parameters testing into the procedure.

Fiber selection was accomplished based on the analyte recovery from three types of commercial SPME fibers including 100 μm PDMS, 75 μm CAR/PDMS, and 65 μm PDMS/DVB. These fibers were selected based on their applicability for the extraction of volatile and nonpolar compounds (Risticvic et al. 2010). Desorption time and temperature in the injector were also optimized in their levels (200, 240, and 280 $^{\circ}\text{C}$ for temperature and 1, 1.5, and 2 min for time). There was no difference in observed recovery between different times and temperatures. Therefore, all fibers were thermally desorbed at 280 $^{\circ}\text{C}$ for 2 min to reduce the potential of carryover of heavy compounds during consecutive sampling. The extraction time profile was prepared for fibers by fully exposing them in the dynamic test chamber. PERC reached equilibrium state after about 60 min in the dynamic-exposed mode with CAR/PDMS (Fig. 2). Equilibrium was reached

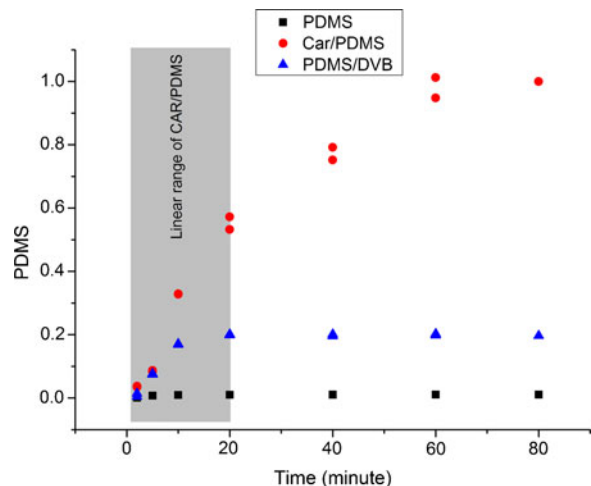


Fig. 2 Extracted mass with three-fiber coating (all measurements were performed in 50 ppmv concentration, 25 ± 0.5 $^{\circ}\text{C}$ and 30 ± 5 % relative humidity for 5 min). All data are normalized relative to the CAR/PDMS measurements

within less than 10 min for PDMS/DVB and PDMS fibers. CAR/PDMS was finally chosen because of its better extraction rate compared to the PDMS and PDMS/DVB fibers.

CAR/PDMS extraction profile was also studied in 0.5-cm retracted mode to determine its adsorption capacity for TWA sampling of PERC. Results showed that the profile is linear up to 240 min at four times the threshold limit value (TLV, 100 ppmv) ($r^2=0.998$). Sampling under this concentration for 360 min showed deviation from the linear pattern. It seems that under this condition, the adsorption isotherm reach its plateau. Therefore, 0.5-cm retracted CAR/PDMS fiber was selected for further developments.

Sampling rate of CAR/PDMS fiber in the retracted mode was calculated theoretically and experimentally by the procedure described in air sampling section. Binary gas phase diffusion coefficient (based on FSG method) and theoretical sampling rate were $4.45 \text{ cm}^2/\text{min}$ and $7.72 \times 10^{-3} \text{ cm}^3/\text{min}$, respectively. Actual sampling rate calculated in this way was $6.43 \times 10^{-3} \text{ cm}^3/\text{min}$ that is slightly less than the theoretical value. Results also showed that there was no change in sampling rate after 240-min sampling in 100 ppmv (Fig. 3). However, the sampling rates in the first 15 min of sampling were slightly higher than (but not statically significant) those observed in longer times. It seems that sorption of analyte on the stainless steel needle led to this difference.

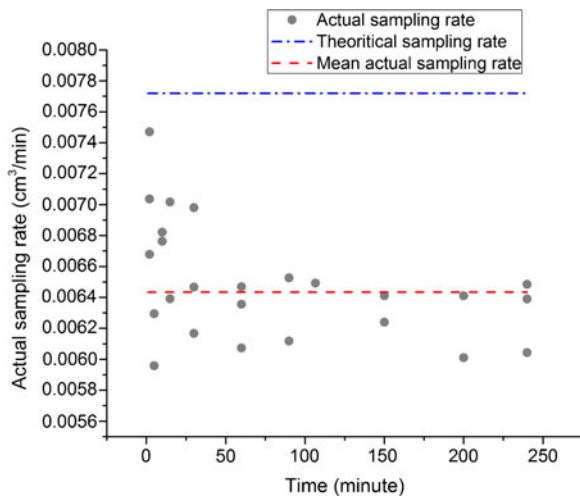


Fig. 3 Actual sampling rate (SR_a) of 0.5 cm retracted CAR/PDMS in various sampling times

Environmental parameters

Dry cleaning shops are high humidity environments with elevated temperature in comparison with other working environments. Therefore, in the development of sampling methods for application in such environments, it is feasible to consider the effect of environmental parameters like air temperature, velocity, and RH on the sampler performance.

Extraction time profile of PERC in 0.5-cm retracted mode was studied at three different temperatures (20, 25, and 30 °C). Table 1 shows the sampling rate of the CAR/PDMS fiber in 0.5-cm retracted mode in different temperatures. Statistical comparison of the results showed that ± 5 °C difference in temperature doesn't have a significant effect on the sampling rate in the range of 5 to 240-min sampling time (p value >0.05), but change of temperature at 10 °C has a significant effect on sampling rate (p value <0.05) in the same conditions. According to Eq. 1, sampling rate is directly proportional to the diffusion coefficient and the diffusion coefficient is proportional to the temperature by $T^{1.085}$. Based on this assumption, it is proven that change of temperature in the range of 10 °C only leads to 4 % displacement in measurements (Wang et al. 2009). Therefore, it seems that temperature variation in the range of 10 °C is not crucial for calibration of the SPME sampler.

Effect of air humidity on the sampling rate was studied in the range of 30 to 80 % at three levels (30, 50, and 80 % at 25 °C). Results showed humidity

has a significant negative effect on sampling rate of the sampler. It may be because of the competition between the analyte and water molecules for the adsorption sites (Koziel et al. 2000). Besides this finding, some other researchers found that humidity doesn't have any significant effect on the properties of the SPME samplers. It seems that this behavior is not similar for all types of analytes and the effect of RH on sampling rate is dependent on the polarity of the analytes and the SPME coating, as well as analyte volatility (Chen et al. 2006). The sampling time might also be important as more and more water molecules can be adsorbed with time. In this study, all humidity tests were performed for 30 min in 50 ppmv concentration.

Effect of air velocity on sampling rate of CAR/PDMS in retracted mode was studied in the range of 0 (static condition) to 50 cm/s. This range was chosen based on the results of the study conducted by Baldwin and Maynard (1998) which stated that mean air velocity in 85 % of the workplaces is below 30 cm/s. ANOVA and Tukey's test were performed to examine the effect of velocity on the sampling rate. Results showed that air velocity has no significant effect on the sampling rate of the SPME sampler in 0.5-cm retracted mode ($p>0.05$). However, the sampling rate of the SPME sampler in static mode was significantly lower than the values observed in dynamic mode (Table 1).

Method validation

Repeatability of the developed method was checked by sampling under the same conditions by one fiber (sampling time: 1 h, 100 ppmv, $n=6$). Results showed that relative standard deviation (RSD) of SPME samples under this condition is 8.9 %. Reproducibility of the method was investigated in the field by exposing six fibers simultaneously in the same conditions close to each other. Results showed that reproducibility of the proposed method in the field varied from 7 % to 11 %. It seems that turbulent currents in the workplace lead to much higher variation in the results. Amagai and Matsushita (1999) proposed a passive sampling method for groups of organohalogenes including PERC with 2.5 % reproducibility which is much better than SPME. However, the SPME reproducibility in the laboratory and field is much better in comparison with the NIOSH 1003 which is about 15.1 % (Eller and Cassinelli 1994).

Table 1 Effect of environmental parameters on CAR/PDMS fiber sampling rate in 0.5-cm retracted mode (temperature in °C, humidity in relative scale %, velocity in cm/s)

Parameter	Level	Mean	SD	Minimum	Maximum	<i>F</i>	<i>P</i> value
Temperature	20	6.41	0.312	6.23	6.84	0.581	0.588
	25	6.32	0.187	6.24	6.61		
	30	6.33	0.280	6.14	6.65		
Humidity	30	6.51	0.367	6.09	6.82	14.77	0.005
	50	5.65	0.243	5.48	5.93		
	80	5.13	0.258	4.86	5.38		
Velocity	0	5.8	0.062	5.73	5.83	2.87	0.081
	0.05	6.37	0.424	6.08	6.93		
	0.1	6.43	0.234	6.25	6.69		
	0.3	6.65	0.519	6.20	7.22		
	0.5	6.34	0.209	6.13	6.55		

The detection limit of the developed method was calculated as an amount of analyte spiked on the sampler which will give a response that is significantly different from the background response of a blank. The detection limit reported by OSHA for PERC sampling and analysis by charcoal is 0.35 µg. It is 0.66 µg for SKC 575–002 samplers (OSHA 1999). The minimum detection limit of PERC for SPME in 0.5-cm retracted mode was 0.08 ng per sample for 4-h samples which is significantly better than the value proposed by the NIOSH 1003 method.

Storage condition

Effect of storage time and condition on the mass recovery of SPME samples was investigated. Samples in this section were taken at 25±1 °C and 45±5 % RH for 5 min at 50 ppmv. SPME samples were stored in three different modes, including (1) septum-capped mode in sealed glass tubes at ambient temperature (18 °C to 23 °C), (2) septum-capped mode in sealed glass tubes at 4 °C, and (3) without septum in sealed glass tubes at ambient temperature. For each storage condition, two samples were taken consecutively by the same SPME fiber. The first was analyzed immediately, and the other was analyzed after the storage time. In this study, we defined good storage ability if at least 90 % recovery was achieved.

The best recovery was obtained for the capped SPME fibers in a glass tube which was stored in 4 °C. Sample loss was much higher in the samples

stored in the ambient temperature. The samples stored at 4 °C could be stored without any significant losses for up to 7 days (up to 92 % recovery). However, septum capping doesn't have a significant effect on sample loss for perchlorethylene. According to this finding, we only continue this test for 7 days because all of the recoveries fall below 90 % during 7 days of storage. This finding is not as good as the storage conditions from the NIOSH 1003 method reported sample stability up to 30 days (Eller and Cassinelli 1994). However, it seems that in most cases, there is no need to store samples more than 1 week before analysis. There are controversial results about this subject in literatures. The interaction of analyte, fiber coating, and loading concentration may be a determinant factor in the storage ability response of the specific fiber to the specific analyte. However, like this study, Haberhauer, in his work on the sulfur compounds, concluded that the temperature is a critical factor in storage ability of the samples (Haberhauer Troyer et al. 1999). Chen (2004) found that CAR/PDMS storage ability for *n*-alkanes after 8-h sampling is good up to 2 weeks at room temperature. Further studies should be conducted to reveal other important factors affecting the SPME sample storage ability and ways to improve it.

Field sampling

Field applicability of the developed SPME method in comparison with the NIOSH 1003 method was evaluated in one dry cleaning shop in Hamedan City,

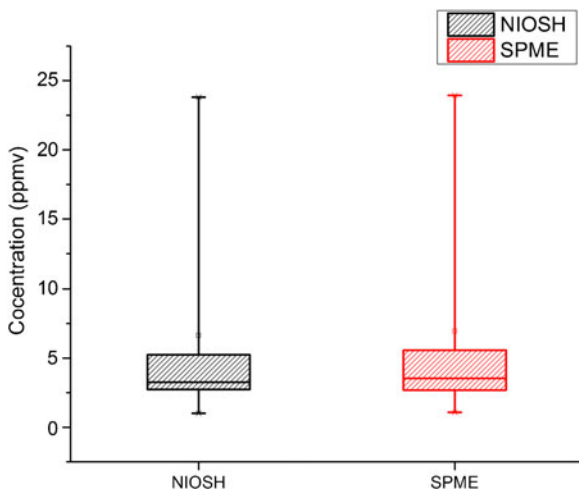


Fig. 4 Whisker plot of the results obtained by SPME and NIOSH method in a dry cleaning shop

located in the western part of Iran. RH and temperature in the shop were measured daily. RH and temperature were in range of 38–43 % and 22–24 °C, respectively. Therefore, the actual sampling rate determined at 25 °C and 40 % RH was used for quantifications. Figure 4 shows a whisker plot of the results obtained by both methods. The linear regression equation for both methods was $NIOSH = 0.972 \text{ SPME} + 0.492$ with $R^2 = 0.978$ ($n = 20$). Table 2 also shows the comprehensive statistical comparison of the field data. According to the prerequisites in industrial hygiene, most of the exposure data have log-normal distribution (Damiano and Mulhausen 1999). Therefore, in the first step, all data was checked by *w* test for normality. Results showed the data acquired by both methods

have log-normal distribution. Only one batch of SPME measurements in the third day doesn't fit to a log-normal distribution. Results showed that there is no statistical difference between the means of daily exposure measured by both methods ($p \text{ value} < 0.05$).

According to the exposure assessment strategy described by the AIHA, five exposure control rating categories were defined based on the proximity of measured data (for example 95th percentile) to the exposure limit (Damiano and Mulhausen 1999). This strategy was used in this article for comparison of the results of the two methods (Fig. 5). Results showed SPME method yields more conservative results than NIOSH 1003 standard method. As can be seen in Table 2, geometric mean determined by SPME method is higher than those determined by NIOSH 1003 in most cases (however, it is not statistically different).

Discussion

The results of this study showed that the developed SPME method based on the proposed procedure could be used effectively for sampling and determination of PERC in occupational environments such as dry cleanings. Application of this easy to use, solventless, small-sized, and cost-effective tool can improve the quality of data gathered by hygienists for exposure assessment purposes. Our findings also revealed that environmental parameters such as ambient temperature and air velocity don't affect significantly the PERC sampling rate in the studied ranges and, therefore, the sampler doesn't need to be calibrated against

Table 2 Statistical comparison of results obtained by developed SPME method and NIOSH 1003 method in a dry cleaning shop

Sampling day	1		2		3		4		5	
	NIOSH	SPME	NIOSH	SPME	NIOSH	SPME	NIOSH	SPME	NIOSH	SPME
Number of samples	4	4	4	4	4	4	4	4	4	4
Maximum	23.81	23.948	3.4911	4.8086	5.3055	6.009	1.233	1.9522	3.2103	3.3589
Minimum	19.859	19.209	2.6919	2.4955	3.3705	5.0271	1.0071	1.0688	2.9889	2.8802
Mean	21.530	21.483	3.065	3.465	4.319	5.302	1.138	1.399	3.097	3.041
Median	21.225	21.388	3.038	3.277	4.300	5.086	1.156	1.287	3.095	2.962
Standard deviation	1.660	1.947	0.395	1.028	1.068	0.474	0.106	0.383	0.098	0.219
Geometric mean	21.483	21.417	3.046	3.355	4.219	5.287	1.134	1.364	3.096	3.035
Geometric standard deviation	1.079	1.095	1.138	1.337	1.286	1.090	1.099	1.290	1.032	1.073
Percent above OEL	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %	0.0 %

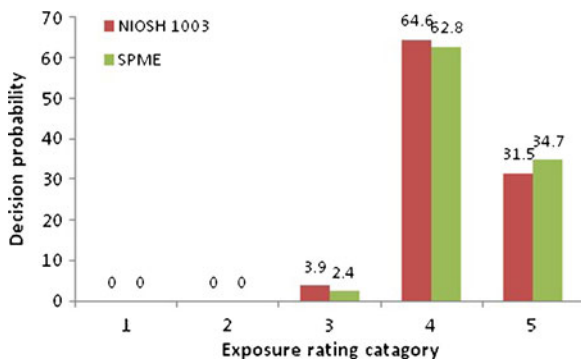


Fig. 5 Exposure rating of both SPME and NIOSH method data based on exposure groups developed by AIHA

these parameters for field quantification purposes. However, further studies should be conducted for a thorough assessment of the SPME sampler response in different exposure scenarios. The data for effect of velocity on sampling rate was gathered in the range of 2 to 50 cm/s and, therefore, could only be applicable in this range of velocity. However, it seems that velocity in most indoor working environments are within this range. Results also showed that RH could be a determining factor in sampler responses and should be considered in quantification of samples. Results of the laboratory side by side sampling and field comparative sampling showed that the developed method is a reliable alternative for traditional sorbent and solvent-based methods.

Analysis of the results according to the AIHA strategy for exposure assessment showed that application of SPME as a sampler leads to slightly more conservative decision making. Its 34.7 % probability to the SPME results were in category 4, but it is 31.5 % for charcoal data. However, this difference is not high but it reveals that the use of conventional statistical methods like regression and regression coefficient may lead to inappropriate reasoning and decision about usefulness of the methods. However, in this study, it is revealed that application of AIHA strategy of exposure banding leads to a more realistic decision about the nature of the sampler.

Conclusion

Use of SPME as a novel sampling device in inhalation exposure assessment has numerous benefits. There are few studies that directly examined SPME as a sampler

for occupational inhalational exposures especially in its diffusive mode for prolonged sampling. In this study, we applied SPME in retracted mode successfully for occupational exposure assessment in one dry cleaning shop. The developed SPME sampler had good response in various environmental conditions in comparison with standard sorbent and solvent-based method. However, there are also other influencing parameters that should be considered in further studies. We propose that future studies focus on the optimization of SPME sample storage ability and also SPME sampler response in dusty environments.

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