

ORIGINAL ARTICLE

Application of Solid Phase Microextraction (SPME) Sampler for Determination of Carbon Disulfide in Air

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ABSTRACT

Carbon disulfide is used predominantly in the manufacture. It has affects the nervous system. In this study, the applicability of SPME as a passive sampler for determination of carbon disulphide in air was studied. Effect of sampler and environmental parameters on uptake of Carbon disulphide was studied as well. Four fibers were tested to select the best sampler for determine carbon disulfide in ambient air. A standard generation chamber was built in the laboratory and was used to test the SPME. Analysis SPME samples were carried out by a gas chromatography-Mass spectrometry and results were compared with data obtained with National Institute for Occupational Safety and Health (NIOSH) method 1600. Polymethylsiloxane-carboxen (PDMS/CAR) showed the most effective stationary phase material for sorbing BTEX among other materials (polyacrylate, PDMS, PDMS/divinylbenzene). Its linearity range in exposed mode was less than 10 minutes but with its retracted mode application, its linearity increased up to 8 hours. Temperature had not linear effect on uptake of pollutant in temperatures lower than 25, it has positive effect and above this range it has negative effect. Relative humidity had negative effect on mass loaded on fiber. Velocity in range of static to 0.5 m/s had no significant effect. The precision of the method was 4.18% relative standard deviation (RSD). The detection limit for carbon disulfide in the GC/MS system in SIM mode was 6.7 ng per sample. SPME is a good alternative for sampling of carbon disulfide in air. However, for the situations in high humidity values it should be used with care.

Keywords: *Carbon disulphide, Air sampling, Gas chromatography, Solid phase microextraction*

INTRODUCTION

Carbon disulfide (CS₂) is an important industrial liquid organic solvent with yellowish liquid of unpleasant odor and widely used for the production of viscose rayon, rubber, and other organic materials. It is a feedstock for the synthesis of sulfuric acid. It is

desirable solvent for most sample extraction processes when the chromatographic analysis should be performed [1].

In human and experimental studies, CS₂ is easily absorbed via inhalation, oral or skin routes and is distributed throughout the body, due to its affinity to lipid rich tissues and organs. There are many reports concerning its toxicity particularly in the peripheral and central nervous systems, cardiovascular system, ophthalmological system, and even the reproductive

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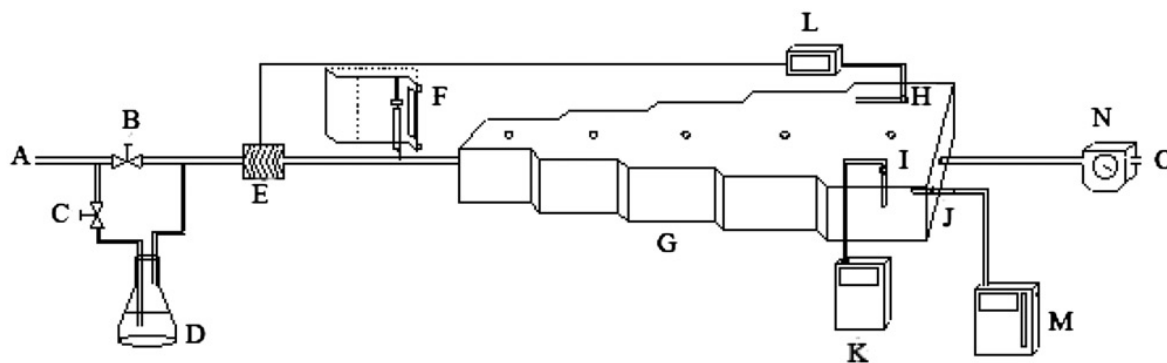


Fig 1. Schematic diagram of test atmosphere generation system. A: Air inlet B: Bypass valve

C: Valve to humidity system D: Humidity generation system E: Electrical coil F: Syringe pump
G: Sampling chamber H: Temperature sensor I: Humidity sensor J: Active sampling port
K: Hygrometer L: Thermocouple M: Personal sampler pump N: Dry gas meter O: Outlet (to hood)

system [2-3]. There are evidences in animal studies that inhalation exposure to this compound can deteriorate brain, spleen, liver and testiness in rats [2]. Workers, which exposed to this compound, are at 2.5 to 5 higher risk of death due to cardiovascular reasons [4-5]. Chronic exposure to carbon disulfide can accelerate the atherosclerosis and acute coronary ischemic disorders [6]. There is also some evidence about its embryotoxicity in animals [7]. Recommended exposure level for these compounds is varied in countries. For example, the Threshold Limit Value (TLV) for the eight-hour Time-Weighted Average (TWA) concentration of CS_2 is 10 ppm as recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). The current Permissible Exposure Limit (PEL) is 4 ppm and TWA (10 h) is 1 ppm, with a Short-Term Exposure Limit (STEL) at 10 ppm by the US NIOSH [8].

The current sampling of carbon disulfide in air is based on using active air sampling with sorbent tubes; extraction by organic solvents, especially carbon disulfide; and analysis by gas chromatography with flame photometric detector (GC-FPD) [9]. 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 [10].

Passive samplers are separate type of samplers which can eliminate the pump from sampling train and therefore are less complicated in nature in comparison with active sampling trains [11]. However, the classic passive samplers also needs some sample extraction steps and therefore needs solvent extractions. Solid phase microextraction (SPME) in its retracted mode is a specific type of passive sampler, which employ diffusion to samples the pollutant. In comparison with classic passive samplers, it is less expensive and solvent free [12]. Analytes in the sample are directly extracted

and concentrated to the extraction fiber. The method saves preparation time and disposal costs and can improve detection limits [12]. It has been routinely used in combination with gas chromatography and GC/mass spectrometry (MS) and successfully applied to a wide variety of compounds, especially for the extraction of volatile and semi-volatile organic compounds from environmental, biological and food samples. It has potential as a rapid air sampling method for volatile organic compounds (VOCs) and as a method for time-weighted average air sampling [12-17]. Based on our knowledge, there is no planned similar study based on application of SPME for determination of carbon disulfide.

The purpose of the current research was to investigate the applicability of SPME as a TWA sampler for carbon disulfide in the air. In the first step, the SPME process was optimized; then the effect of relevant at environmental parameters such as temperature, air velocity and relative humidity on the mass uptake of SPME was studied. Applicability of the proposed method in comparison with the NIOSH 1600 method was examined under laboratory and real conditions.

MATERIAL AND METHODS

Toluene (99.9%) and carbon disulfide (99.9%) 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 obtained from SKC Inc (Eighty Four, PA, USA). SPME fibers, including 100 μm poly dimethylsiloxane (PDMS), 65 μm PDMS/divinylbenzene (PDMS/DVB), 75 μm carboxen/PDMS (CAR/PDMS), and SPME manual holders were purchased 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

Table 1. Effect of environmental parameters on sampling of CS₂

Parameter	Levels	Peak area	Mean	SD
Humidity	20	14078	14451	1186.27
		13496		
		15780		
	40	12756	13298	995.18
		12690		
		14447		
60	11346	10707	668.34	
	10012			
	10763			
Temperature	20	24453	25177	626.56
		25535		
		25542		
	25	31334	30114	1073.78
		29690		
		29317		
30	25463	24325	1104.60	
	23257			
	24256			
Velocity	0.00	25221	23659	1392.90
		23212		
		22545		
	0.06	21833	22560	810.65
		23434		
		22412		
	0.075	23120	23048	615.20
		23624		
		22400		
	0.1	23936	23407	889.50
		22159		
		23122		
0.15	19145	20177	1061.20	
	21265			
	20122			
0.3	22761	20913	1701.17	
	19412			
	20565			

standard atmosphere is thoroughly described in another paper [14].

Analysis of all SPME samples were performed by a gas chromatography-Mass spectrometry model (CP 3800 Supelco, Bellefonte, PA) the GC was equipped with a capillary VOCOL column with 60 m×0.25 mm ID, 1.5 µm film thickness (Supelco, Bellefonte, PA) and helium as a carrier gas (1 ml/min). CS₂ eluted at 7.9 minute. An injector was equipped with 0.85 mm narrow insert liner and was set at 280°C.

The MS transfer line temperature was set at 220°C. Quantification of carbon disulfide was performed in SIM mode at m/z 117. For SPME samples, GC was programmed at 80°C for 1 min and then ramped at 10°C/min to 180°C and held for 1 min. Calibration was performed by calibration curve prepared from liquid standards prepared in toluene in 6 points. GC's calibration was checked every day by injecting a mid-range standard solution. They were recalibrated if the results showed a deviation greater than 5%. Charcoal

tube samples were extracted according to NIOSH 1600, with 0.5 ml carbon disulfide for 30 minutes [9]. All SPME fibers were purchased from Supelco (Bellefonte, Pa.). They consisted of 1 cm length, fused silica fiber bonded to a stainless steel plunger. Several stationary phase materials were tested to select the best fiber for determine carbon disulfide in ambient air. These fibers include: poly (acrylate) (PA), poly (dimethylsiloxane) (PDMS), poly (dimethylsiloxane)/divinylbenzene (PDMS/DVB), and poly(dimethylsiloxane)/Carboxen (PDMS/ CAR). Prior to their first use, all the fibers were conditioned in the GC injector at the temperature (220–320°C) and for the time (0.5–4 h) recommended by the supplier.

A dynamic atmosphere generation system was built in the laboratory (Fig 1). The configuration of the system was suitable for sampling at various air velocities, temperatures, and humidity. The humidity generation system consisted of an impinger, heater and bypass valves for changing airflow rate and temperature

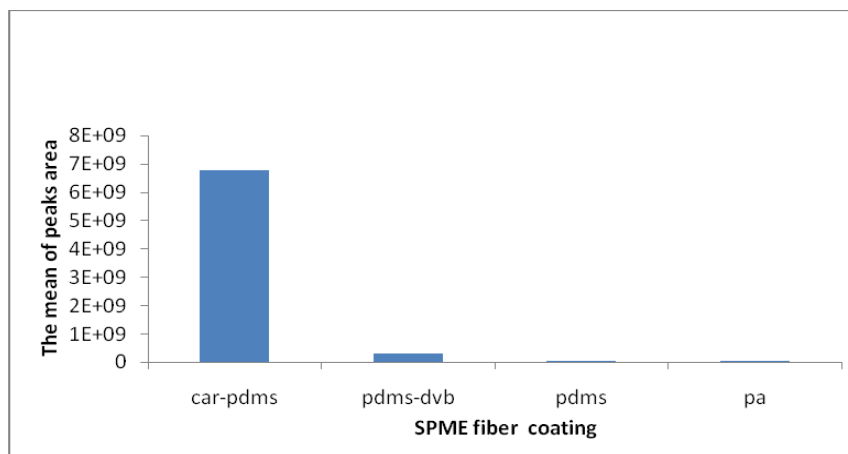


Fig 2. The mean of peak area loading of different SPME fiber coatings in exposed mode

Sampling time: 15 min, 50 ppmv, 18%-3% relative humidity, 25°C sampling temperature, 0.1 m/s air velocity, 2 min desorption time

of water in impinger. Humidity also was monitored by Testo601 hygrometer (Model Testo 601, Testoterm GmbH & Co., Germany). Analyte was delivered to the remixing chamber with syringe pump at predetermined injection rate that selected based on desired concentration, and calculated by follow Equation.

$$Q = \frac{\rho \times 24.45 \times IR \times 1000000}{MW \times C \times 60}$$

That, ρ is the density of analyte that will be injected in g/l, IR is injection rate (ml/h), MW is molecular weight of analyte, C is the desirable concentration in chamber in ppm and Q is diluents gas flow rate (LPM). Concentration in the chamber was changed by simply changing the air flow-rate, or by preparing a different standard mixture with different liquid concentration. It should be noted that calculated concentration in this equation is a rough estimation of concentration and was used only for preliminary determination of desired injection rate, precise determination of concentration in the chamber was made by active sampling and analysis by NIOSH 1600 method.

Laboratory samples were taken from dynamic conditions with SPME fibers in a standard generation chamber. Active sampling was performed according to NIOSH 1600 method for carbon disulfide 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 toluene for 30 min according to procedure described by NIOSH 1600. SPME in this study was used in the retracted mode; therefore, it acts like a passive sampler and quantification can be made based on Fick's first law of diffusion.

$$C = \frac{n \times L}{t \times D_g \times A}$$

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) calculated according to the method described earlier [18]. A is the cross section area of the SPME needle opening (square centimeter) and was measured [13]. 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 $D_g A / L$ 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.

RESULTS

Fibers comparison results showed that the CAR/PDMS is the most sensitive fiber for sampling of CS₂. The PDMS/DVB fiber also had good sensitivity in comparison with two other absorptive fibers (PDMS and PA) (Fig 2). In comparison with CAR/PDMS, has significantly lower sensitivity. In exposed mode, the CAR/PDMS also reaches equilibrium state in about 5 minutes (Fig 3-a). From these results, the authors selected CAR/PDMS as a gold fiber for further analysis. For further developments, adsorption isotherm of CAR/PDMS in exposed and retracted mode was studied in different time intervals. Results showed that in the retracted mode the CAR/PDMS has significantly greater linearity range. In retracted mode, the CAR/PDMS isotherm for CS₂ was linear up to 480 minutes (Fig 3-b).

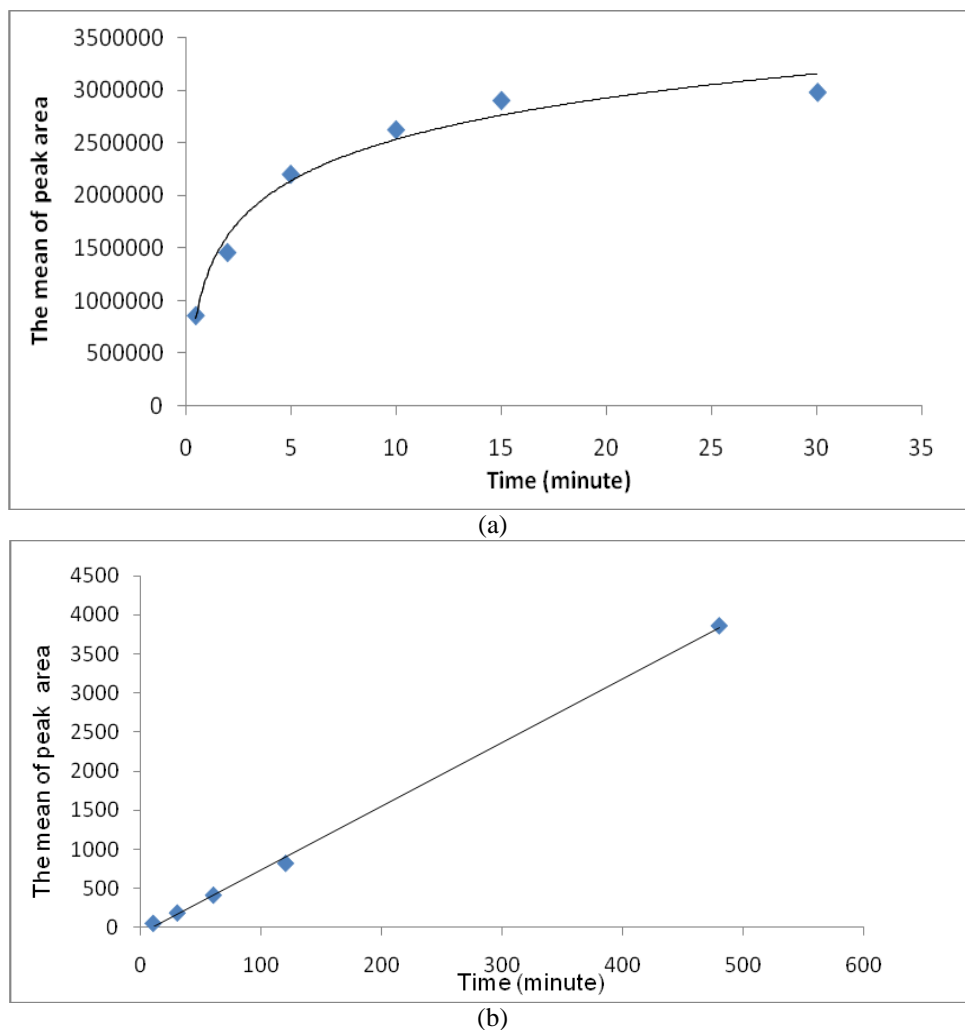


Fig 3. Extraction profile of carbon disulfide a) exposed mode b)retracted mode

Effect of sampling temperature on uptake of CS_2 was measured in three levels include 20, 25, 30°C. This range was selected because it is prevalent and most probable air temperature in the work environments. Air velocity in temperature tests was considered at 0.1 m/s and the relative humidity was set at 37%. With an increase in the temperature from 20°C to 25°C, the extraction efficiency of CAR/PDMS for CS_2 will increase significantly (Table 1). With further increase in temperature up to 30°C, the extracted amount of CS_2 dropped significantly.

Effect of air velocity on uptake of CS_2 in SPME was studied in retracted and exposed mode at 25°C and 21-27% relative humidity (Table 1). Velocity was studied in 5 levels from nearly static conditions to about 0.5 m/s. In both exposed and retracted modes, there was no difference between the analyte uptakes in different air velocities and the data from exposed mode showed higher variations in comparison with retracted mode. Velocity measurements in exposed mode showed that in higher velocities, the variability (measured as a standard

deviation of measurements) increased. The sampling was repeated three times.

Effect of relative humidity on uptake of pollutant was studied in three levels in range of 20-60 (20, 40, 60%) at 0.1 m/s (Table 1). The sampling was repeated three times for each humidity level. With an increase in relative humidity, the analyte extraction dropped significantly. Minimum detection limit of CS_2 was calculated as a concentration with the signal to noise ratio of greater than three. For CAR/PDMS SPME in retracted mode the minimum detection limit is about 6.7ng. Side by side measurements showed that the SPME was a reliable sampler for CS_2 .

The coconut charcoal tube was used to carry out the comparative test with SPME fiber. The coconut charcoal tube contained 100 mg of charcoal in the sample section and 50 mg in the backup section. These experimental conditions were chosen so that the amount of carbon disulfide component absorbed by the charcoal tubes corresponds more or less to the LOD estimated at 10 μg per tube. The charcoal tubes were extracted with

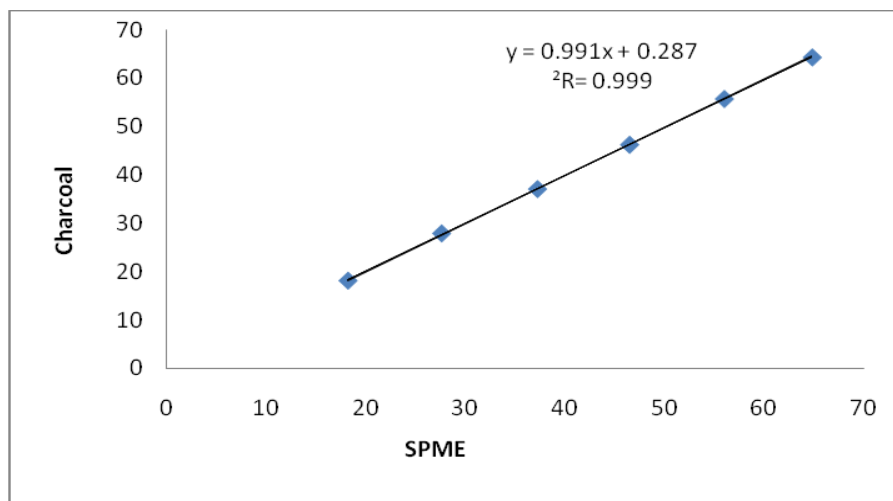


Fig 4. Regression line for measurements with SPME and NIOSH 1600 method

toluene (0.5 ml) prior to GC injection (1 μ l). Triplicate measurements were carried out with each charcoal tubes concentration level. The results were then compared with data obtained with the use of a SPME fiber coated with the selected polymer phase (Fig 4). The fiber was exposed for 10 min to the generated atmosphere at 0% RH, under gas flow ranging from 0.3 to 3.0 l/min.

As for sensitivity, the limit of detection (LOD) and the limit of quantification (LOQ) were calculated according to the recommendations of the EURACHEM Guide (2002) [19]. This method used the equations $LOD = \text{mean of sample blank} + 3S$, and $LOQ = \text{mean of sample blank} + 10S$, where S is the standard deviation for 10 repetitions of the extraction procedure with the sample blank. The LOD for carbon disulfide in the GC/MS system in SIM mode was 6.7ng per sample. It is good in comparison with the LOD proposed by NIOSH 1600method, which is about 0.03 mg per sample. Repeatability of SPME method was studied by taking six samples under similar conditions for 15 minutes at 10 ppmv, 25°C and 30% RH. It was about 4.18% for carbon disulfide.

DISCUSSION

Results of this study showed that SPME is a valuable tool in sampling and determination of CS₂ in air. It is in agreement with other studies. However, some other studies reported that it has some difficulties in sample preservation [16]. We found application of SPME in exposed mode for extended times has some drawback. It also suffers from breakthrough in situations with high concentration. It is the feature of adsorptive fibers like CAR/PDMS [20]. With application of this method in retracted mode, it is possible to extend the isotherm linearity range and therefore extend the sampling time [21]. As can be seen from Fig. 2, the isotherm in exposed mode reached semi

equilibrium state only after three minutes. After 15 minutes this isotherm reached nearly equilibrium state, it implies that the net mass transfer between fiber and media is zero in this condition.

Our results showed that for the situations that the short time sampling is preferred; application of retracted mode is not suitable. It is also advisable to use absorptive fibers in the cases with short time sampling. However, the sensitivity of absorptive fibers is lower than the adsorptive ones. Therefore, it is suitable to perform sampling with absorptive fibers in exposed mode. With considering worldwide exposure limit of CS₂ in range of 1-10 ppmv [8], it is possible to use SPME for most situations even in concentrations several times higher than the exposure limits.

In general, environmental parameters like temperature, velocity and relative humidity have significant effect on mass uptake on passive samplers [14-15]. Results of prior studies showed that environmental parameters affect the sampling rate and in other word mass transfer of pollutant on the fibers [21]. Application of the fibers in the exposed mode increases the confounding role of environmental factors in pollutant transfer to the fiber. Therefore, it should be calibrated truly for these situations.

CONCLUSION

SPME is a good alternative for regular exposure assessment purposes. Relative humidity decorates the uptake of CS₂. It should be used carefully in high humidity environments. Further studies should be conducted to examine the adsorption isotherm of CS₂ in different psychrometric conditions. SPME is a good alternative for solvent and sorbent-based methods. However, there is also lack of field application and comparison. We suggest that further studies should be

conducted in the field to compare the SPME method with sorbent and solvent-based methods.

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