

Evaluation of Indoor Exposition to Benzene, Toluene, Ethylbenzene, Xylene, and Styrene by Passive Sampling with a Solid-Phase Microextraction Device

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Abstract

A solid-phase microextraction (SPME) sampling method is developed to evaluate indoor exposure to benzene, toluene, ethylbenzene, xylene, and styrene with gas chromatography and flame ionization detection for quantitative analysis. An SPME holder with a 100- μm polydimethylsiloxane (PDMS) and 65- μm PDMS–divinylbenzene fiber coating is tested in different air relative humidity conditions. The method gives good resolution, shows a linear response, is repeatable, and presents high sensitivity. This method is compared with National Institute of Occupational Safety and Health (NIOSH) active sampling.

Introduction

The monitoring of internal atmospheres is very important because a large number of potentially hazardous volatile organic compounds are produced or used indoors. Benzene, toluene, ethylbenzene, *m*-xylene, *o*-xylene, *p*-xylene, and styrene (BTEXS) are residues present in most solvents.

The method most commonly used to determine low-concentration organic compounds in internal atmospheres is calculating the average concentration over a period of time (time weighted–average concentration) with passive or active sampling to adsorb the gas on a solid and a later analysis of the components by gas chromatography (GC). There are three types of passive samplers: tube, badge, and radial. Active-sampling methods draw air through a sampling tube by means of a pump.

Passive sampling is advantageous to active sampling because

it does not require a careful calibration routine and expensive air-sampling pumps. However, potentially faulty batteries tend to present constant hurdles to the air-sampling professional, and samplers are affected by ambient pressure and temperature changes during sampling (1–3). Also, passive-sampling devices are currently expensive and are not reusable. High humidity can alter the sorption capacity of a sorbent or the sorption behavior of the exposed inner wall of tube-type samples if condensation occurs (4).

A single solid-phase microextraction (SPME) device is an attractive alternative to conventional passive-sampling methods (5–9) because this technique is fast, economical, and the fiber is reusable.

This study presents an efficient method to determine indoor exposition to BTEXS by GC analysis with a flame ionization detector (FID) and an SPME sampling device. Experiments with polydimethylsiloxane (PDMS) and PDMS–divinylbenzene (DVB) fibers were carried out at different air relative humidity conditions. The fiber that presented the best result in this study was subjected to experiments to determine the equilibrium time, linearity range, repeatability, and detection limit (LOD). In addition, analyses of real samples were carried out in parallel with the National Institute of Occupational Safety and Health (NIOSH) 1501 method.

Experimental

Chemicals and materials

BTEXS were obtained from Merck (Darmstadt, Germany). Carbon disulfide (CS_2) was obtained from Riedel-de Haën (Seelze, Germany). Activated charcoal (20–35 mesh), magnesium chloride hexahydrate, sodium chloride, potassium chloride, and potassium nitrate were also obtained from Merck. The

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stock standard solution of BTEXS was prepared in a concentration of 1000.0 mg/L using CS₂ as a solvent. Intermediate concentration solutions were prepared according to experimental conditions.

The nitrogen, hydrogen, and synthetic air for FID and the synthetic air for the standard gas generation device were obtained from White Martins (Belo Horizonte, Brazil). The synthetic air had a water concentration below 1 ppm.

The SPME holder with 100- μ m PDMS and PDMS-DVB 65- μ m-fiber assemblies were purchased from Supelco (Bellefonte, PA).

Equipment

The chromatographic analyses were performed using an HP 5890 Series II GC (Hewlett Packard, Avondale, PA) equipped with an FID.

The analyses were carried out in an HP Ultra 1 capillary column (cross-linked phenyl methylsiloxane film) with a 50-m length and a 0.20-mm i.d. with a 33- μ m phase thickness. The oven temperature program for GC began at 35°C and was then raised to 125°C at 10°C/min and then to 250°C at 20°C/min. The carrier gas was hydrogen at a flow rate of 0.90 mL/min at 100°C. A 0.75-mm-i.d. SPME insert was used in the split/splitless injector selected in the splitless mode at 220°C.

The detector was set at 280°C in the analysis with the GC-FID system.

Humidity generation

The system used for the dynamic generation of humidity with stopped flow was based on Nelson's system (10) and is illustrated in Figure 1. The "dry air" is a gas stream prepared using compressed air and scrubbers. The humid air was generated by passing a dry-air flow through water flask 6. The different humidity values inside of flask 10 were obtained by varying the proportion of dry air and humid air. The baths for the generation of humid air (flask 6) and the mixture/measurement chamber (flask 8) were maintained at 30°C. In order to obtain the desired humidity value, the required proportion of dry air and humid air was flushed through chamber number 8 for 10 min. Shortly thereafter, the vacuum

pump was turned down and the humidity reached equilibrium in approximately 10 min. After measuring the humidity value with a TESTO (Lenzkirch, Germany) Model 635 hygrometer (flask 9), the air with known humidity was carried through a stainless steel tube with an outer diameter of 0.56 mm to the sampling chamber (flask 14).

Standard gas generation

The static generation of the standard mixture was carried out in a stirrer/heater with an aluminum block containing a 22-mL Pyrex vial (Supelco) (as illustrated in Figure 1). The vials were calibrated and sealed with aluminum caps containing Teflon-rubber septa.

The standard gaseous mixture of BTEXS was obtained through the injection of the standard liquid inside the vial with a 5.00-mL Hamilton (Reno, NV) syringe. Then, the vial was left in the system (described in Figure 1) for 30 min at 30°C \pm 0.5°C to generate the standard gas with a known relative humidity. A stirring bar of 14 \times 5 mm at 1000 rpm was used to homogenize the standard gas generated. After 30 min of homogenization, stirring was stopped and the fiber was introduced into the vial for the sorption of the analytes. The BTEXS compounds were desorbed in the injector for 3 min at 220°C.

The theoretical concentration was calculated in parts per million for volume (ppm_v) at 25°C and 1 atm using the equation:

$$\text{ppm}_v = (24.5 \times 10^6 \times W) / (V \times M) \quad \text{Eq. 1}$$

where *W* is the weight of the compound (g), *V* the volume of the sample in the vial (L), and *M* the molecular weight of the compound (g/mol).

Results and Discussion

Evaluation of the PDMS and PDMS-DVB fibers in different humidity conditions

The concentration of standard gas mixtures used to study the effect of humidity on analyte sorption by SPME fibers were

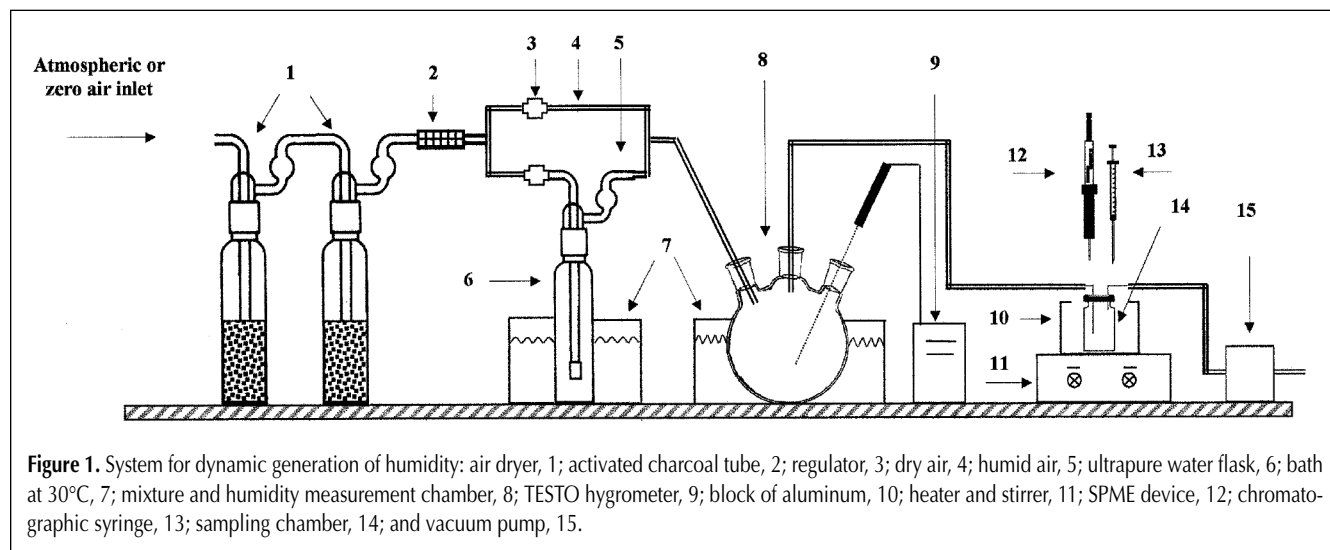


Figure 1. System for dynamic generation of humidity: air dryer, 1; activated charcoal tube, 2; regulator, 3; dry air, 4; humid air, 5; ultrapure water flask, 6; bath at 30°C, 7; mixture and humidity measurement chamber, 8; TESTO hygrometer, 9; block of aluminum, 10; heater and stirrer, 11; SPME device, 12; chromatographic syringe, 13; sampling chamber, 14; and vacuum pump, 15.

1.43, 1.20, 1.00, 1.05, 1.07, and 1.05 ppm_v for benzene, toluene, ethylbenzene, *m*- and *p*-xylene, styrene, and *o*-xylene, respectively, at 25°C and 1 atm.

The effect of relative humidity on the sorption of BTEXS using PDMS and PDMS-DVB is plotted in Figures 2 and 3, respectively. The results obtained with both fibers indicated that the sorption of each BTEXS compound remained nearly the same at different humidity values. Therefore, humidity appeared not to interfere with fiber sorption.

The PDMS-DVB fiber had a high BTEXS sorption capacity in relation to the PDMS fiber. This sensitivity can be observed through the area values of Figures 2 and 3. Therefore, the results obtained supported the choice of the PDMS-DVB fiber for BTEXS sampling in ambient air.

PDMS-DVB equilibrium time

The development of an SPME method requires the determination of the minimum time necessary for the analytes to reach equilibrium between a gaseous mixture and the PDMS-DVB fiber. For this purpose, the PDMS-DVB fiber was exposed to the gas standard mixtures in concentrations of 1.43, 1.20, 1.00, 1.05, 1.07, and 1.05 ppm_v for benzene, toluene, ethylbenzene, *m*- and *p*-xylene, styrene, and *o*-xylene, respectively, at 25°C and 1 atm. The fiber was exposed for the following times: 0.25, 1, 5, 15, 30, and 60 min. These experiments were carried out with atmospheric air in a relative humidity of 46% ± 2%. The results are plotted in Figure 4. The equilibrium time was relatively fast (approximately 1 min for benzene and toluene and 5 min for ethylbenzene, *m*- and *p*-xylene, styrene, and *o*-xylene). Accordingly, the time of 5 min was used in the partial validation experiments.

SPME methods

The linearity study is summarized in Table I. Although the correlation coefficients were in a range of 0.992 and 0.999, the analysis of variance indicated that there was a linear relationship between concentration and area. The relationship between the regression average square (QM_{reg}) and the residue average square (QM_r) was larger than the tabulated F value for 1.4 df (F = 7.71). Concentrations of benzene, toluene, ethylbenzene, *m*- and *p*-xylene, styrene, and *o*-xylene over 45.62, 38.68, 32.04, 33.57, 33.57, and 34.22 ppm_v, respectively, at 25°C and 1 atm did not present a linear relationship between the concentration and area. In

the adsorption extraction process, the isotherm is highly non-linear for higher concentrations when the surface coverage is substantial (11).

The repeatability experiment of the PDMS-DVB fiber was carried out through the sampling and analysis of two ranges of different concentrations of the standard gas samples. The first range of concentration (data 1) was 0.07 ppm_v for benzene; 0.06 ppm_v for toluene; and 0.02 ppm_v for ethylbenzene, *m*- and *p*-xylene, styrene, and *o*-xylene. In the second range (data 2), the values of concentration were 22.81, 19.34, 16.02, 16.78, 17.11, and 16.78 ppm_v for benzene, toluene, ethylbenzene, *m*- and *p*-xylene, styrene, and *o*-xylene, respectively. These analyses were

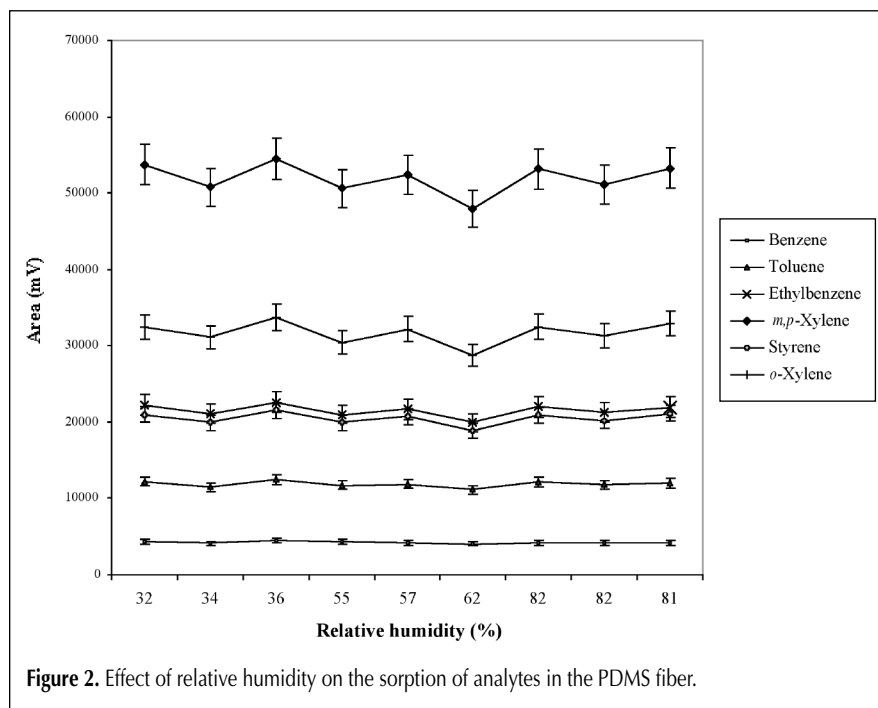


Figure 2. Effect of relative humidity on the sorption of analytes in the PDMS fiber.

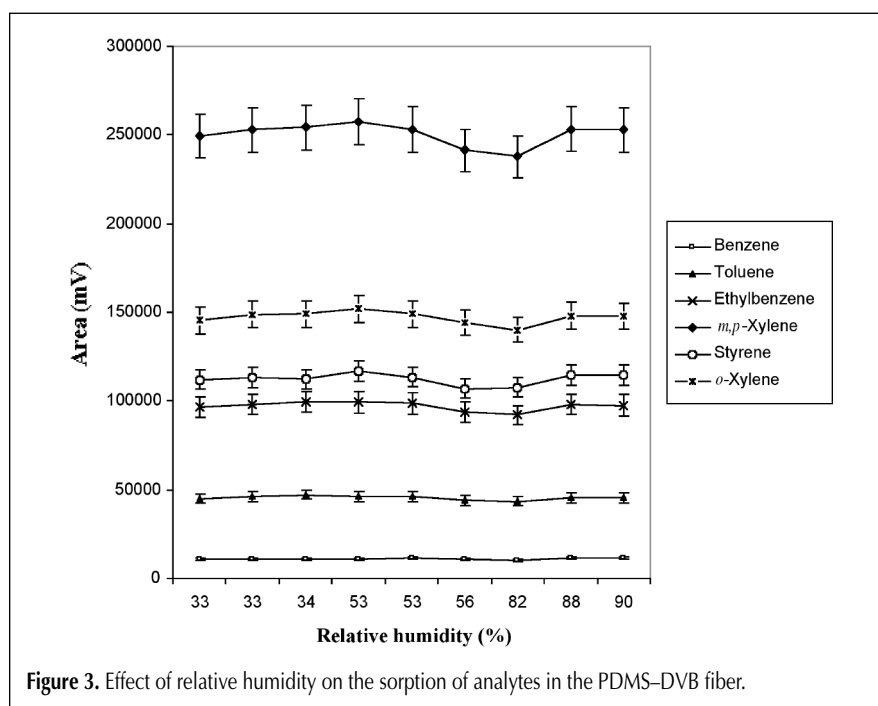


Figure 3. Effect of relative humidity on the sorption of analytes in the PDMS-DVB fiber.

carried out in the same laboratory by the same operator using the same apparatus over a relatively short time span (same day). The results (summarized in Table II) indicate that this standard gas generation device, combined with sampling by PDMS–DVB fibers, is precise for equilibrium sampling conditions.

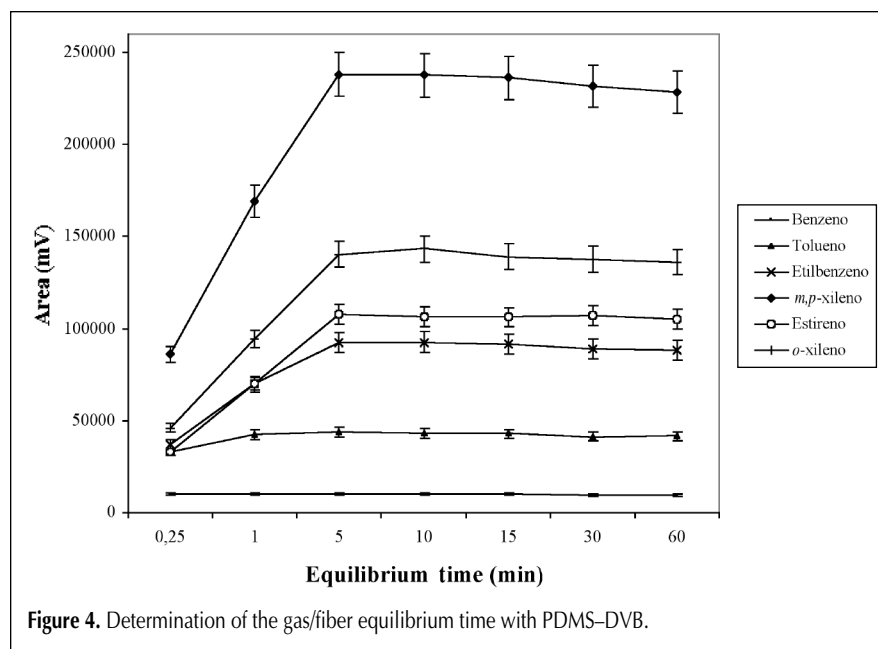


Figure 4. Determination of the gas/fiber equilibrium time with PDMS–DVB.

Table I. Linear Regression Analysis Parameters* of BTEXS in the SPME–GC Method

Analyte	Range (ppm _v)	Equation	R [†]	QM _{reg} /QM _r
Benzene	0.07–45.62	$y = 1045x + 2037$	0.997	809.20
Toluene	0.06–38.6	$y = 4287x + 5949$	0.999	2061.61
Ethylbenzene	0.02–32.04	$y = 10432x + 14049$	0.997	640.54
<i>m</i> - and <i>p</i> -Xylene	0.02–33.57	$y = 24610x + 39735$	0.995	449.70
<i>o</i> -Xylene	0.02–33.57	$y = 23778x + 32339$	0.997	611.34
Styrene	0.02–34.22	$y = 19039x + 38924$	0.992	241.71

* These experiments were carried out with atmospheric air in a relative humidity of 46% ± 2% at 30°C and a PDMS–DVB fiber.

† R, correlation coefficient.

Table II. Analysis Parameters* of Repeatability and MDL of BTEXS in the SPME–GC Method

Analyte	Repeatability (%RSD)		MDL (ppb _v)
	Data 1	Data 2	
Benzene	5.7	8.9	16.70
Toluene	7.0	4.7	20.07
Ethylbenzene	6.3	5.3	3.33
<i>m</i> - and <i>p</i> -Xylene	5.9	4.1	3.45
<i>o</i> -Xylene	5.9	3.8	3.03
Styrene	5.7	4.4	3.51

* These experiments were carried out with atmospheric air in a relative humidity of 46% ± 2% at 30°C and a PDMS–DVB fiber.

The results of the method detection limit (MDL) are summarized in Table II. The MDL was determined through the sampling and analysis of seven gas standards (12). The statistical results obtained for this series of analyses were substituted into the equation:

$$\text{MDL} = t_{(N-1, 1-\alpha=0.99)} \times S_c \quad \text{Eq. 2}$$

where t is the student value for $N - 1$ degrees of freedom to 99% confidence and S_c is the standard deviation of the seven analyses.

Analysis of real samples

The application of the SPME method was carried out in indoor air passive sampling at two fuel analysis laboratories (A and B) and in an office with wet latex paint. The SPME sampling was made in parallel with NIOSH method 1501 (13). Integrated samples were collected for a period of 180 min. The sampling time was long in order to verify the emission of new analytes in the indoor air and because the BTEXS concentration in air was very low for the NIOSH method. After the sampling period, the fiber and cartridge were refrigerated to 3°C for 1 h until analysis time (14). Then, the cartridges described in NIOSH method 1501 and the PDMS–DVB fibers were desorbed in the injector for 3 min at 220°C. The results were determined from calibration curves.

The analysis by the NIOSH method did not detect any compound of the BTEXS group in laboratories A and B. In the office, the NIOSH method and the SPME method had similar determinations for the compounds detected. The LOD of NIOSH method 1501 is 0.001 for 0.01 mg. The results (shown in Table III) indicate that SPME with a PDMS–DVB fiber is

more sensitive than NIOSH at trace quantities of analytes in the sampling conditions used.

Conclusion

This study proposes a method for the passive sampling of BTEXS in indoor air with an SPME device. The sorption study of the PDMS and PDMS–DVB fibers in different relative air humidity conditions shows that the fibers do not suffer from interference in the large range of humidity of BTEXS sampling. The PDMS–DVB fiber was selected because it presented higher sorption capacity. Analysis of real samples was made to compare the classic active-sampling and the SPME passive-sam-

Table III. Analysis of Real Samples* with the NIOSH Active-Sampling Method and SPME Passive-Sampling Method Using a PDMS–DVB Fiber

Sampling Place	Day	Toluene (ppm _v)		Ethylbenzene (ppm _v)		<i>m</i> - and <i>p</i> -Xylene (ppm _v)		<i>o</i> -Xylene (ppm _v)	
		SPME	NIOSH	SPME	NIOSH	SPME	NIOSH	SPME	NIOSH
Laboratory A	1	2.74	n.d.	0.61	n.d.	0.21	n.d.	0.09	n.d.
	2	1.77	n.d. [†]	0.80	n.d.	0.28	n.d.	0.13	n.d.
	3	3.06	n.d.	0.27	n.d.	0.43	n.d.	0.20	n.d.
	4 [‡]	1.41	n.d.	0.11	n.d.	0.17	n.d.	0.07	n.d.
Laboratory B	–	1.19	n.d.	0.24	n.d.	0.35	n.d.	0.15	n.d.
Office	–	n.d.	n.d.	n.d.	n.d.	13.93	10.39 [§]	15.42	16.91 [§]

* Temperature and relative humidity were 27°C and 57% ± 3%, respectively.

[†] n.d., not detected (below LOD).

[‡] Sampling time was 8 h. Average flow of 130 mL/min and 180 min.

pling method. This comparison shows that the SPME method is economical and capable of achieving a very low LOD. Because of the advantages of the SPME passive-sampling method, this technique can be used for the quantitative analysis of BTEXS indoor exposition.

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