

## Determination of Volatile Organic Compounds (VOCs) Using Tedlar Bag/Solid-phase Microextraction/Gas Chromatography/Mass Spectrometry (SPME/GC/MS) in Ambient and Workplace Air

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*Received November 12, 2001*

SPME techniques have proven to be very useful tools in the analysis of wide VOCs in the air. In this study, we estimated VOCs in ambient and workplace air using a Tedlar bag/SPME/GC/MS system. The calibration curve was set to be linear over the range of 1-30 ppbv. The detection limits ranged from 10 pptv to 0.93 ppbv for all VOCs. Reproducibility of TO-14 target gas mixtures by SPME/GC/MS averaged at 8.8 R.S.D (%). Air toxic VOCs (hazardous air pollutants, HAPs) containing a total of forty halohydrocarbons, aromatics, and haloaromatic carbons could be analyzed with significant accuracy, detection limit and linearity at low ppbv level. Only reactive VOCs with low molecular weight, such as chloromethane, vinylchloride, ethylchloride and 1,2-dichloroethane, yielded relatively poor results using this technique. In ambient air samples, ten VOCs were identified and quantified after external calibration. VOC concentration in ambient and workplace air ranged from 0.04 to 1.85 ppbv. The overall process was successfully applied to identify and quantify VOCs in ambient/workplace air.

**Keywords :** VOCs, Tedlar bag, GC/MS, Solid-phase microextraction (SPME), Detection limit.

### Introduction

Volatile organic compounds (VOCs) in ambient air originate from various biogenic and anthropogenic sources.<sup>1</sup> The US Clean Air Act Amendments (CAAA) of 1990 lists 189 chemicals as hazardous air pollutants (HAPs), and nearly 100 of them have been classified as VOCs.<sup>2</sup> This class of compounds typically has boiling points in the range of 50-260 °C<sup>3</sup> and vapour pressures greater than 0.1 torr.<sup>4</sup> Exposure to low-level VOC concentrations in indoor air is suspected to contribute to a variety of non-specific symptoms such as headache, and eye, nose and skin irritations, which are categorized as part of "sick building syndrome".<sup>5</sup>

The 1990 CAAA and California Safe Drinking Water and Toxic Enforcement Act of 1986 require a large number of various VOCs to be monitored.<sup>6</sup> The majority of the methods developed for VOCs in air have been canister-based<sup>7-9</sup> or sorbent-based,<sup>10-13</sup> and or polymeric bag.<sup>14-16</sup> In canister-based methods, a whole air sample is drawn into a metal canister, and a portion of it is then analyzed using methods that involve passing the air through either a cryotrap or a sorbent bed, thereby focusing the VOCs prior to analysis using gas chromatography (GC). In the sorbent-based method, an air sample is pulled directly through a glass or metal tube that is packed with an appropriate sorbent material. Thermal desorption is usually used to transfer the analytes to the GC column. In both canister and sorbent-based methods, samples can not be directly analyzed without the application of preconcentration and sample pretreatment techniques because the concentration of analytes is lower than the detection limit.<sup>17</sup> Thus, it is necessary to perform

sample preparation steps prior to analysis. Conventional measures of preconcentration involve using cryogenics such as liquid nitrogen, argon, or CO<sub>2</sub> to condense VOCs onto some inert solid surface as air sample flowing through.<sup>18</sup> However, these analytical methods require various sample preparation steps, and preconcentration devices such as cryotrap and peltier cooler system, and as such, they are also time-consuming.

Recently, a new extraction technique called solid-phase-microextraction (SPME) has been developed by Pawliszyn *et al.*<sup>19-20</sup> In this technique, sampling, extraction and concentrations are incorporated into a single step and the use of solvents, where possible environmental pollutants may reside, is eliminated. A fused-silica fiber, coated with a polymer, is exposed to the gaseous sample or immersed in an aqueous sample to extract the analytes.<sup>21-25</sup> The fiber is then injected into the gas chromatography injection port for thermal desorption and analysis.

SPME is based on partition equilibrium of the analytes between the aqueous or gases sample and the polymer coating of a fused-silica fiber.<sup>26</sup> In normal operation, the fiber is exposed to the sample media until equilibrium is reached, but the time needed to reach the adsorption equilibrium between the sample and the polymer coating can be very long. In these situations, shortening the adsorption time and working in non-equilibrium conditions are desirable.<sup>27</sup>

Extensive studies on the SPME technique, including theory, optimization, its automation and the dynamics of adsorption, as well as a number of applications have been summarized in a recent book.<sup>28</sup> SPME has been applied to

the analysis of different compounds including polynuclear aromatic hydrocarbons (PAHs) and polychlorinated hydrocarbons,<sup>27,29</sup> volatile chlorinated hydrocarbons,<sup>30</sup> phenols,<sup>31-33</sup> pesticides,<sup>34-47</sup> organoarsenic compounds,<sup>48</sup> organotin compounds,<sup>49</sup> fatty acids,<sup>50</sup> tetraethyllead,<sup>51</sup> volatile carbonyl compounds,<sup>52</sup> trimethylamine,<sup>53</sup> drugs<sup>54</sup> and volatile organic compounds (VOCs).<sup>55-62</sup>

This study reported to evaluate a wide range of VOCs by /SPME/GC/MS system using a Tedlar bag. A collection of VOCs, chosen as good representatives of the entire class of VOCs, is listed in the EPA method TO-14 (see Table 1). These groups include representatives of all classes of VOCs: freons, trihalomethanes as well as other halogenated compounds, and aromatic and haloaromatic compounds. GC/MS analysis of VOCs was carried out using a capillary column after ambient/workplace air was collected on the Tedlar bag, and were then extracted using SPME

### Experimental Design

**Chemicals and materials.** TO-14 Standard gas mixture cylinder (forty VOCs in nitrogen) was purchased from Matheson Gas Products (San Francisco, CA). The information on target VOCs is listed on Table 1. The Tedlar bag (1 and 5 L) was supplied by SKC (SKC, USA). The gas-tight syringes (1, 10 and 50 mL) were supplied by Graf FORTUNA (Germany), while the 2 L gas syringe was obtained from Hamilton (MODEL S-2000, Reno, Nevada, USA). A DCI-NA type air sampler was obtained from Japan.

**SPME fibers.** The SPME holder for manual sampling was purchased from Supelco. Polydimethylsiloxane (PDMS) (100  $\mu\text{m}$  film thickness), polyacrylate (PA) (85  $\mu\text{m}$  film thickness), Carboxen-PDMS (CAR/PDMS) (75  $\mu\text{m}$  film thickness), and Carbowax-divinylbenzene (CW/DVB) (65  $\mu\text{m}$  film thickness) fibers were obtained from Supelco (Bellefonte, PA, USA). Four fibers were tested and compared. All the SPME fibers were conditioned in the hot injector portion of the gas chromatograph according to instructions provided by the supplier.

**Standard preparation and GC/MS analysis.** Analytical gas standards were prepared using volumetric injection. A known amount of TO-14 standard gas mixture was loaded into 1 L Tedlar bag through a septum using a gas-tight syringe. After the sample preparation, the SPME syringe needle was inserted into a Tedlar bag filled with standard gas mixture through a septum. The CAR/PDMS SPME fiber was then lowered into the standard gas by depressing the plunger. Target VOCs were partitioned into the polymeric coating of the fiber until equilibrium was reached. The plunger was then withdrawn, and the needle was removed from the standard gas Tedlar bag. After extraction for 15 min, the fiber was directly exposed for 5 min at 250 °C in the GC injector. Thermal desorption of analytes was carried out for 3 min. The environmental air samples (real sample) were obtained in 5 L Tedlar bag. The environmental air samples in the Tedlar bag then were extracted using the same procedure followed in SPME extraction from a standard gas Tedlar

bag.

Analyses were carried out on a Varian 3400 CX gas chromatograph (GC), which was connected to a Varian Saturn 2000 mass spectrometer. Ionization mode of mass spectrometer was EI (electron impact) at 70 eV. The mass range scanned was from  $m/z$  35 to 280 amu. The gas chromatograph/mass spectrometer interface temperature was 200 while the ion source temperature was 195 °C. The GC injection port was maintained at a temperature of 250 °C for thermal desorption. Separation was carried out on a 60 m  $\times$  0.32 mm  $\times$  1  $\mu\text{m}$  DB-1 capillary column (J & W Scientific, USA), while column oven temperature was initially held at 40 °C for 4 min, programmed to 190 °C at a rate of 7/min, and then to 250 °C at 10 °C/min. The sample was quantified by selected ion monitoring (SIM). Quantification of the ions ( $m/z$ ) is shown in Table 1. High-purity helium (99.995%) was used as a carrier gas at a flow-rate of 1 mL/min. Outlet split flow and septum purge flow was 10 mL/min and 3 mL/min, respectively.

**Storage stability of target VOCs in Tedlar bag.** 1-liter Tedlar bag was used to compare the stability of target VOCs over a 46 h period (5 Tedlar bags: zero air using a high purity nitrogen gas matrix, other 5 Tedlar bags: 25% humidified with a real air matrix). The target VOCs were prepared along with concentrations of 30 ppbv and stored in room temperature (exactly 19 °C). The storage test was conducted over a 46 hour period, with analysis at 0, 3, 6, 20, and 46 h. The Tedlar bags were vacuumed to remove air, water vapor, and any organic compounds before use.

**Application to ambient/workplace air.** The Tedlar bag has long been used in sampling and analyzing source emissions for pollutants. It was one of the recommended sampling techniques in the EPA method 18<sup>63</sup>. The samples were collected using a 5 L Tedlar bag during rush hours at the road and in an organic laboratory. Ambient/workplace air samples were drawn through 5 L Tedlar bag using a DCI-NA type air sampler, operating at a flow-rate of 500 mL/min. The relative humidity of ambient and workplace (organic laboratory) air sample was 33% and 44%, respectively. After ambient/workplace air was sampled, the SPME fiber was then exposed to the air sample for 15 min and directly exposed to the hot injector of the GC system for analysis. Thermal desorption of the target VOCs was carried out at 250 °C.

### Results and Discussion

**Identification of target VOCs by GC/MS.** A comparison of total ion chromatogram between the selected ion monitoring (SIM) and scan mode is illustrated in Figure 1. The SIM mode gave sharper chromatographic peaks for target VOCs than the scan mode. Scan mode analysis did not produce a satisfactory sensitivity at 1 ppbv. In trace analysis, GC/MS scan mode was usually difficult for the determination analysis in the complex matrix. All the experiments were carried out by SIM mode in the quantitative analysis.

Only reactive VOCs with low molecular weight, such as chloromethane, vinylchloride, ethylchloride and 1,2-dichloro-

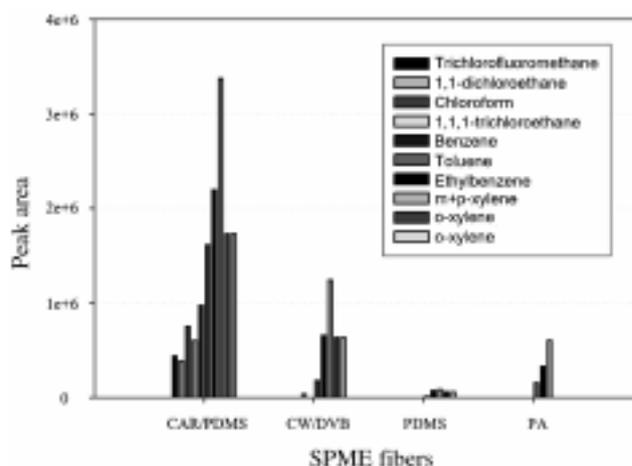
ethane, showed relatively poor results when Tedlar/SPME technique was used. These compounds were not detected within the range of the calibration curve.

**Selection of SPME fiber.** PDMS, PA, CAR/PDMS and CW/DVB coatings are commercially available for SPME. PDMS coating can be applied in non-polar organic compounds such as VOCs, polycyclic aromatic hydrocarbons, benzene, toluene, ethylbenzene, xylene, organochlorine pesticides.<sup>64</sup> PA coating is applicable to polar organic compounds such as triazines, organophosphorous pesticides and phenols.<sup>64</sup> CAR/PDMS coating can be applied to VOCs and hydrocarbons. CW/DVB is applicable for polar organic compounds such as alcohols, ketones, nitroaromatics.<sup>64</sup>

The sensitivity and selectivity of the four types of coating to extract target VOCs from samples were evaluated at 10 ppbv, and the results were illustrated by plotting GC peak area with different type of SPME fibers (Figure 2). The four types of fibers used in this experiment are as follows: 75  $\mu\text{m}$  CAR/PDMS, 65  $\mu\text{m}$  CW/DVB, 100  $\mu\text{m}$  PDMS, and 85  $\mu\text{m}$  PA. Total ion chromatogram obtained at 10 ppbv using four different SPME fibers are shown in Figure 3.

The 75  $\mu\text{m}$  CAR/PDMS fiber proved to be most effective for target VOCs. However, the PDMS and polyacrylate (PA) fiber revealed to have low affinity for all VOCs. The decreasing order of affinity is as follows: 75  $\mu\text{m}$  CAR/PDMS, then 65 100  $\mu\text{m}$ , CW/DVB, 100  $\mu\text{m}$  PDMS and, finally, the 85  $\mu\text{m}$  polyacrylate fiber.

**Equilibrium of target VOCs.** To determine the optimum extraction time, intervals of 5, 10, 15, 20, 25, 30, 35, 40 and 45 min were tested and compared. The extraction time was monitored by plotting the peak area against adsorption time. The equilibrium was not reached until according to our time-adsorption profile for target VOCs. Equilibrium was not reached even after 45 min owing to the large affinity of

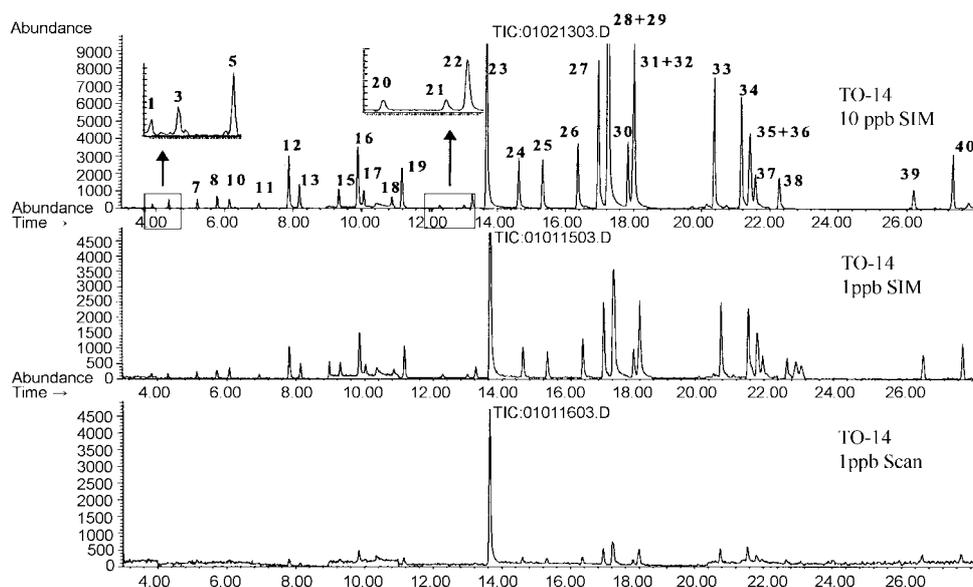


**Figure 2.** Relative extraction efficiency for selected VOCs at 10 ppbv using four SPME fibers (75  $\mu\text{m}$  CAR/PDMS, 65  $\mu\text{m}$  CW/DVB, 100  $\mu\text{m}$  PDMS, 85  $\mu\text{m}$  PA).

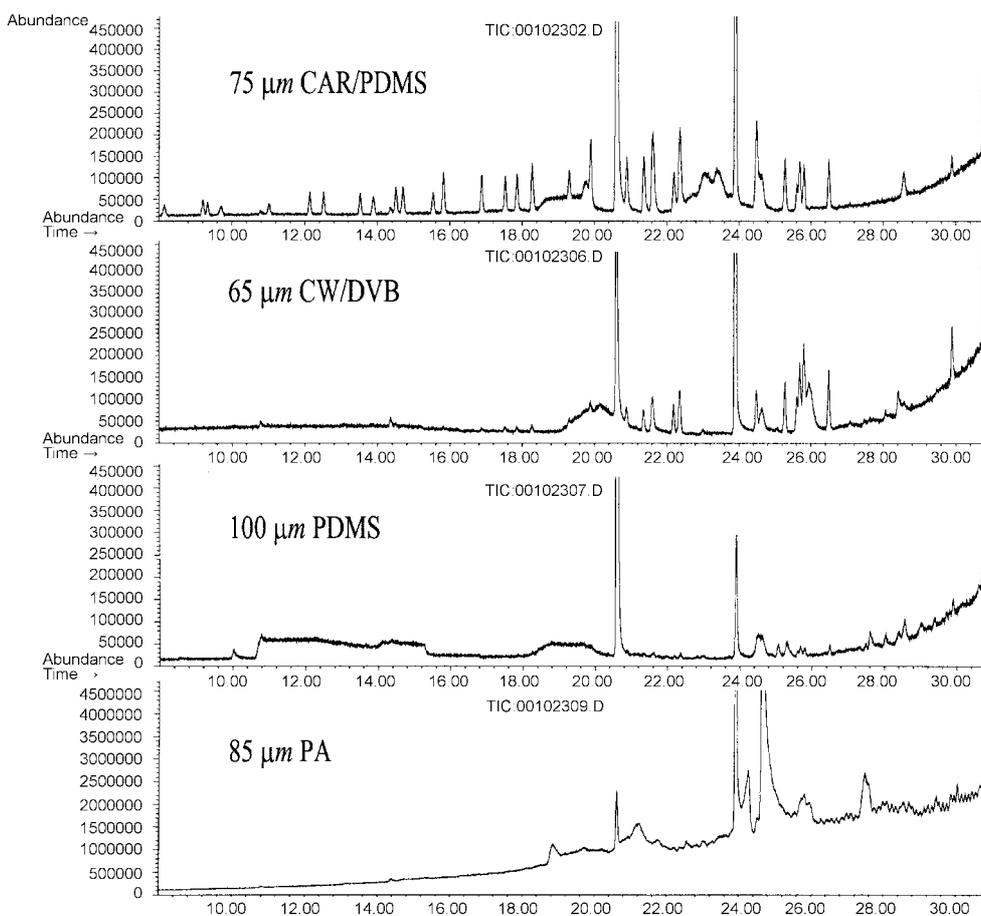
compounds towards the CAR/PDMS fiber. An extraction time of 15 min was selected although equilibrium was yet to be reached at this time. For routine analysis, it was not necessary to reach a complete equilibrium as long as the exposure time of the fiber was kept exactly constant. Detailed results are shown in Figure 4.

Carryover (memory effect) for 15 min adsorption of target VOCs in SPME fiber did not appear in these conditions. This was evaluated by desorbing the same fiber for the second time after the first desorption at hot GC injector.

**Calibration curves and detection limit.** Forty target compounds selected are listed in Table 1. They represent various groups of VOCs which are ubiquitous components in ambient air. To demonstrate the reliability of this SPME technique method, precision, correlation coefficients and



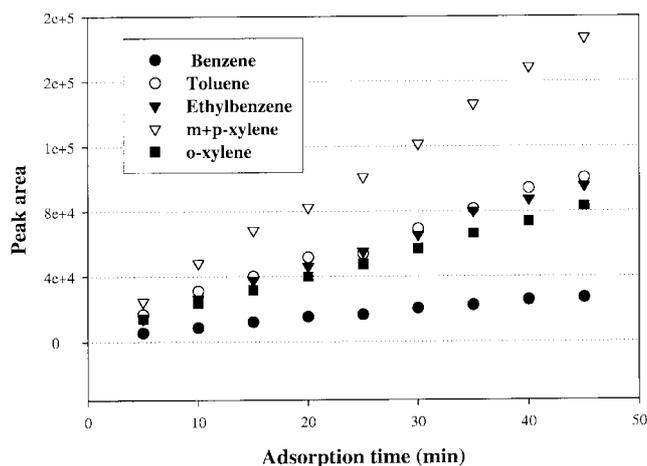
**Figure 1.** Total ion chromatogram of forty VOCs standard obtained from 10 ppbv concentration by GC/MS-SIM mode. The numbers of VOCs were as listed in Table 1.



**Figure 3.** GC/MS chromatogram of the target VOCs by comparison of selectivity and sensitivity: 75  $\mu\text{m}$  CAR/PDMS; 65  $\mu\text{m}$  CW/DVB; 100  $\mu\text{m}$  PDMS; 85  $\mu\text{m}$  PA.

detection limits were determined using Tedlar bag/SPME. The calibration for all target VOCs was linear with a correlation coefficient of at least 0.990 except 1,2-dichloro-1,1,2,2-tetrafluoromethane (0.948) over the range of 1-30 ppbv. Detection limit values for target VOCs were shown from 10 pptv to 0.93 ppbv. The detection limit was estimated to be greater than 3 on the basis of the S/N ratio. The precision obtained, expressed as relative standard deviation, was lower than 10% when Tedlar bag/SPME method was used. Three replicate analysis for calibration of target VOCs standard gas was done in this study. Four compounds namely, chloromethane, vinylchloride, ethylchloride and 1,2-dichloroethane, were not detected in the range of 1-30 ppbv. Detailed results for all VOCs were summarized in Table 1.

**Storage stability in Tedlar bag.** Evaluating temperature and relative humidity is very important in extracting target VOCs using an SPME fiber. Chai *et al.* reported that humidity and temperature cause the amount of analytes adsorbed in the fiber coating to change significantly.<sup>65</sup> They concluded that relative humidity only reduces the amount extracted at room temperature by less than 10% at up to 75% relative humidity. They also reported that the lower the temperature and humidity, the more analytes are adsorbed by



**Figure 4.** Extraction time profile for selected VOCs at 10 ppbv using a 75  $\mu\text{m}$  CAR/PDMS SPME fiber.

the SPME fiber coating.

The results of storage stability at different matrix conditions in this study using a 1 L Tedlar bag revealed a very similar stability for target VOCs. There was no significant difference between high purity nitrogen gas matrix and real air matrix at 20  $^{\circ}\text{C}$ .

**Table 1.** Lists of US EPA TO-14 VOCs, limit of detection and linearity for target compounds by Tedlar bag/SPME/GC/MS.

No	Compounds	R.T (min)	Q ions	RSD (%) (n=3)	LOD <sup>a</sup> (ppbv)	r <sup>2</sup>
1	Dichlorodifluoromethane	3.71	85	7	0.18	0.9950
2	Chloromethane	— <sup>b</sup>	—	—	—	—
3	1,2-Dichloro-1,1,2,2-tetrafluoromethane	3.96	135	9	0.27	0.9476
4	Vinylchloride	—	—	—	—	—
5	Bromomethane	4.44	94	7	0.19	1.0000
6	Ethyl chloride	—	—	—	—	—
7	Trichlorofluoromethane	5.28	101	1	0.02	0.9992
8	1,1-Dichloroethene	5.86	96	5	0.15	0.9998
9	Methylene chloride	5.95	49	32	0.93	0.9964
10	1,1,2-Trichloro-1,2,2-trifluoroethane	6.22	151	11	0.32	0.9949
11	1,1-Dichloroethane	7.13	63	4	0.50	0.9997
12	<i>cis</i> -1,2-Dichloroethylene	7.95	61	19	0.03	1.0000
13	Chloroform	8.26	83	6	0.01	0.9995
14	1,2-Dichloroethane	—	—	—	—	—
15	1,1,1-Trichloroethane	9.41	97	5	0.14	0.9991
16	Benzene	9.96	78	9	0.01	0.9984
17	Carbon tetrachloride	10.14	117	14	0.39	0.9994
18	1,2-Dichloropropane	10.96	76	6	0.16	0.9968
19	Trichloroethylene	11.26	130	2	0.05	0.9999
20	<i>cis</i> -1,3-Dichloropropene	12.38	75	9	0.24	0.9993
21	<i>trans</i> -1,3-Dichloropropene	13.09	75	3	0.07	0.9992
22	1,1,2-Trichloroethane	13.34	97	8	0.19	0.9978
23	Toluene	13.76	91	6	0.01	0.9996
24	1,2-Dibromoethane	14.71	109	2	0.01	0.9995
25	Tetrachloroethylene	15.41	166	4	0.01	0.9987
26	Chlorobenzene	16.45	112	9	0.22	0.9998
27	Ethylbenzene	17.05	91	7	0.01	0.9996
28+29	<i>m+p</i> -Xylene	17.33	91	14	0.02	0.9999
30	Styrene	17.93	104	3	0.01	0.9979
31	1,1,2,2-Tetrachloroethane	18.06	83	26	0.03	0.9999
32	<i>o</i> -Xylene	18.10	91	14	0.02	0.9995
33	1,3,5-Trimethylbenzene	20.46	105	11	0.01	1.0000
34	1,2,4-Trimethylbenzene	21.26	105	5	0.01	0.9997
35	Benzylchloride	21.50	91	19	0.02	0.9993
36	<i>m</i> -Dichlorobenzene	21.53	146	3	0.08	0.9999
37	<i>p</i> -Dichlorobenzene	21.68	146	21	0.02	0.9987
38	<i>o</i> -Dichlorobenzene	22.37	146	17	0.02	0.9990
39	1,2,4-Trichlorobenzene	26.32	180	20	0.02	0.9967
40	Hexachloro-1,3-butadiene	27.45	225	19	0.01	0.9997

<sup>a</sup>3 replicate analysis. <sup>b</sup>not detected in the range of 1-30 ppbv (calibration range)

In the air matrix, styrene, benzyl chloride and 1,2,4-trichlorobenzene yielded a significant loss in 50 h. Styrene showed that a 22% loss in the first 2 h while an additional 43% was lost in the next 50 h. Benzyl chloride yielded loss of 22% in the first 2 h while an additional 40% was lost in the next 9 h. Similarly, 31% of the 1,2,4-trichlorobenzene was lost in the first 2 h while an additional 43% was lost in the next 9h. Dichlorobenzenes (ortho, meta and para-) revealed a loss of 14% in the first 2 h while an additional 27% was lost in the following 9 h. These results indicate that these compounds cannot be stored for a long period probably because of diffusion through the Tedlar bag wall or adsorption onto it. However, BTEX compounds (benzene, toluene,

ethylbenzene and *m,p*-xylenes) proved very stable while the other target VOCs manifested an average loss of 17% in 50 h. Detailed results of storage stability are shown in Figure 5.

**Application of field sampling (ambient air and workplace air).** SPME was applied to real sample (ambient/workplace air) using the same conditions employed in calibrating the method. GC/MS chromatogram results for real samples are shown in Figure 6. Ten VOCs were detected in ambient air. BTEX compounds (benzene, toluene, ethyl-benzene and *m+p*-xylene), trimethylbenzene and trichloro-benzene were found to be important pollutants. VOC concentration detected in ambient air ranged from 0.16 to 1.85 ppbv.

GC/MS chromatogram results for workplace air revealed a

very similar pattern to that of ambient air. Nine VOCs were detected in workplace air. VOC concentration in workplace air ranged from 0.04 to 1.22 ppbv. A summary of all the results is shown in Table 2.

### Conclusions

Various VOCs were estimated using a common GC/MS

system with Tedlar bag /SPME without classical solvent consumption for sample preparation or using cryogenic technique for concentration in ambient/workplace air. A linear working range of 1-30 ppbv was established. Calibration yielded a linear curve over this range except 1,2-dichloro-1,1,2,2-tetrafluoroethane. This method showed a precise average of 8.8% relative standard deviation. Detection limits ranged from 10 pptv to 0.93 ppbv. VOCs with low molecular

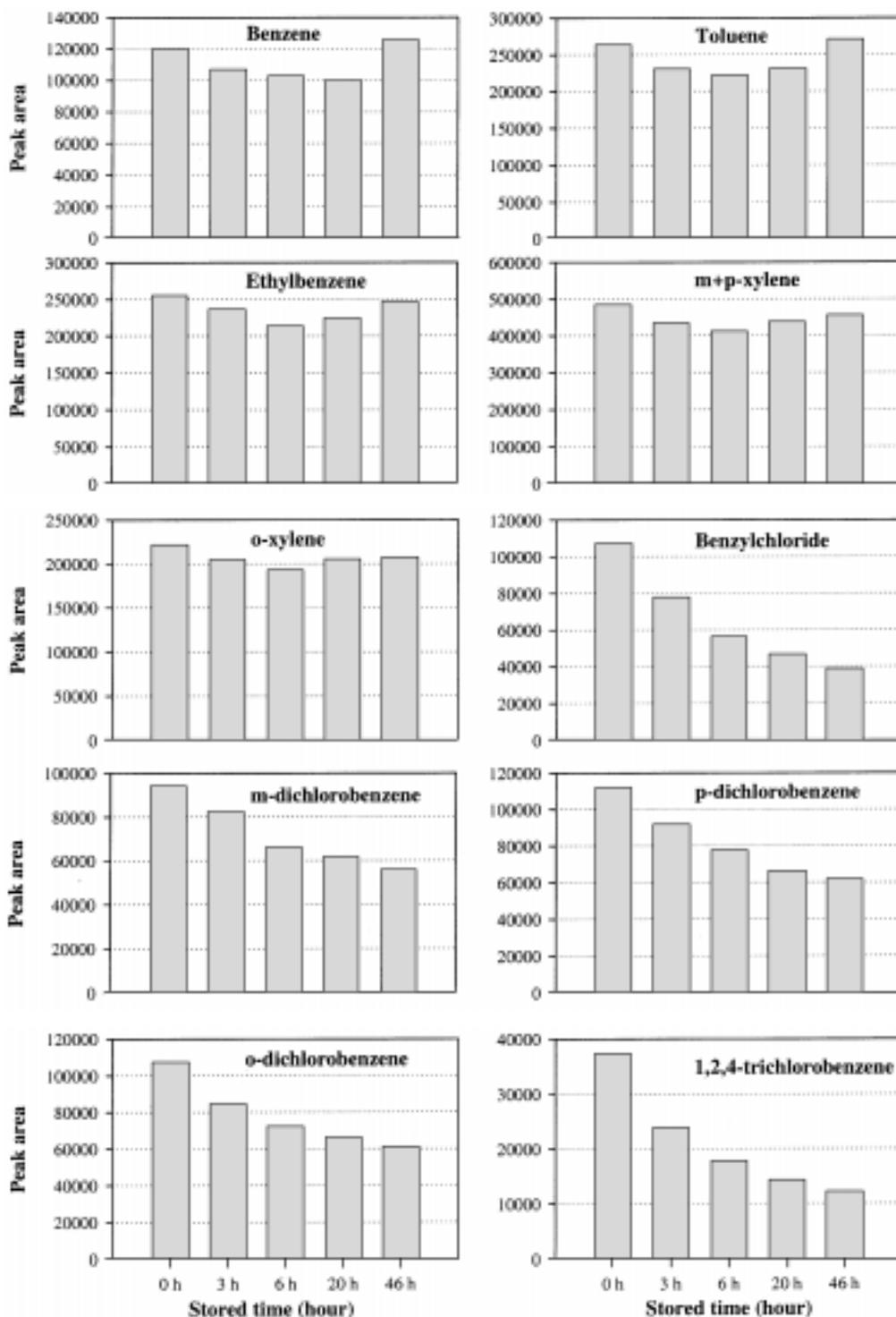
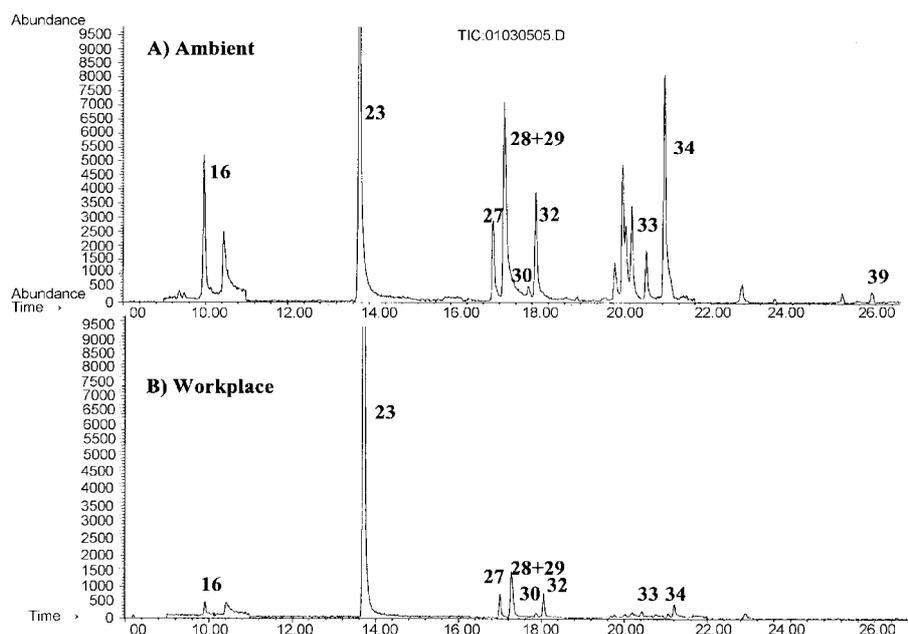


Figure 5. Stability of selected VOCs in 1 L Tedlar bag with real air matrix (RH 25%) at 30 ppbv.



**Figure 6.** (A) GC/MS-SIM chromatogram of VOCs extracted from ambient air using SPME fiber 75  $\mu$ m CAR/PDMS. Analytes in order of elution were: (16) benzene, (23) toluene, (27) ethylbenzene, (28+29) m+p-xylene, (32) *o*-xylene, (33) 1,3,5-trimethylbenzene, (34) 1,2,4-trimethylbenzene, (39) 1,2,4-trichlorobenzene. (B) GC/MS-SIM chromatogram of VOCs extracted from workplace. Analytes in order of elution were: (16) benzene, (23) toluene, (27) ethylbenzene, (28+29) m+p-xylene, (32) *o*-xylene, (33) 1,3,5-trimethylbenzene, (34) 1,2,4-trimethylbenzene.

**Table 2.** The results of concentration in ambient and laboratory air

No	Compounds	M.W. (g/mol)	VOC standard gas conc. (ppmv) <sup>a</sup>	Conc. (ppbv) <sup>b</sup>	Conc. (ppbv) <sup>c</sup>
1	Dichlorodifluoromethane	120.91	0.88	N.D. <sup>d</sup>	N.D.
2	Chloromethane	50.49	0.88	–	–
3	1,2-Dichloro-1,1,2,2-tetrafluoromethane	170.93	0.95	N.D.	N.D.
4	Vinylchloride	62.50	0.92	–	–
5	Bromomethane	94.94	0.89	N.D.	N.D.
6	Ethyl chloride	64.52	0.91	–	–
7	Trichlorofluoromethane	137.38	0.95	N.D.	N.D.
8	1,1-Dichloroethene	96.95	0.92	N.D.	N.D.
9	Methylene chloride	84.94	0.93	N.D.	N.D.
10	1,1,2-Trichloro-1,2,2-trifluoroethane	187.38	0.90	N.D.	N.D.
11	1,1-Dichloroethane	98.96	0.88	N.D.	N.D.
12	<i>cis</i> -1,2-Dichloroethylene	96.94	0.89	N.D.	N.D.
13	Chloroform	119.38	0.90	N.D.	N.D.
14	1,2-Dichloroethane	98.96	0.89	–	–
15	1,1,1-Trichloroethane	133.41	0.90	N.D.	N.D.
16	Benzene	78.12	0.90	0.30	1.85
17	Carbon tetrachloride	153.82	0.90	N.D.	N.D.
18	1,2-Dichloropropane	112.99	0.89	N.D.	N.D.
19	Trichloroethylene	131.29	0.88	N.D.	N.D.
20	<i>cis</i> -1,3-Dichloropropene	110.97	0.85	N.D.	N.D.
21	<i>trans</i> -1,3-Dichloropropene	110.97	0.85	N.D.	N.D.
22	1,1,2-Trichloroethane	133.41	0.82	N.D.	N.D.
23	Toluene	92.15	0.83	1.22	0.78
24	1,2-Dibromoethane	187.88	0.82	N.D.	N.D.
25	Tetrachloroethylene	165.83	0.81	N.D.	N.D.
26	Chlorobenzene	112.56	0.83	N.D.	N.D.

Table 2. Continued

No	Compounds	M.W. (g/mol)	VOC standard gas conc. (ppmv) <sup>a</sup>	Conc. (ppbv) <sup>b</sup>	Conc. (ppbv) <sup>c</sup>
27	Ethylbenzene	106.17	0.80	0.21	0.62
28+29	<i>m+p</i> -Xylene	106.17	0.81	< DL <sup>e</sup>	0.77
30	Styrene	104.16	0.84	0.45	0.56
31	1,1,2,2-Tetrachloroethane	167.85	0.82	N.D	N.D
32	<i>o</i> -Xylene	106.17	0.82	0.15	0.55
33	1,3,5-Trimethylbenzene	120.20	0.74	0.04	0.58
34	1,2,4-Trimethylbenzene	120.20	0.72	0.15	1.82
35	Benzylchloride	126.59	0.82	N.D	N.D
36	<i>m</i> -Dichlorobenzene	147.01	0.70	N.D	N.D
37	<i>p</i> -Dichlorobenzene	147.01	0.69	N.D	N.D
38	<i>o</i> -Dichlorobenzene	147.01	0.57	N.D	N.D
39	1,2,4-Trichlorobenzene	181.45	0.59	N.D	0.16
40	Hexachloro-1,3-butadiene	260.80	0.32	N.D	N.D

<sup>a</sup>VOC standard gas (ppmv concentration) was used for calibration of the analysis. The standard gas was diluted before calibration. Detailed descriptions for dilution are included in context of experimental part. <sup>b</sup>Concentrations of workplace air. <sup>c</sup>Concentrations of ambient air. <sup>d</sup>Not detected. <sup>e</sup>Lower than detection limit.

weight including chloromethane, vinylchloride, ethylchloride and 1,2-dichloroethane were not detected in the calibration range using this technique. VOC concentration in ambient and workplace air ranged from 0.04 to 1.85 ppbv. SPME proved to be a simple, inexpensive, rapid and promising analytical technique for the quantitative analysis of a wide range of VOCs present in ambient/workplace air samples. Tedlar bag/SPME/GC/MS method was proved to be useful for screening of ambient/workplace air.

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