

# Multi-layer Cartridges Filled with Multi-Walled Carbon Nanotubes for the Determination of Volatile Organic Compounds in Indoor Air

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A kind of new multi-layer adsorbent including Tenax TA/multi-walled carbon nanotubes (MWCNTs)/Carboxen 564 was developed for collecting volatile organic compounds. The adsorption and desorption efficiencies of 11 kinds of adsorbents (including Activated charcoal, Tenax TA, Carboxen 564, Chromosorb 101, Chromosorb 102, Chromosorb 103, Chromosorb 105, Porapak Q, GDX 301, XAD-2, and MWCNTs) were compared. By combining the advantages of Tenax TA, MWCNTs, and Carboxen 564, new type of multi-layer adsorbents was developed. The adsorption and desorption efficiency, the sampling reproducibility, and the effect of water were improved using multi-layer adsorbents, Tenax TA/MWCNTs/Carboxen 564. New multi-layer adsorbents were successfully applied to the determination of volatile organic compounds (VOCs) in ambient air.

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## Introduction

In the past few years, volatile organic compounds (VOCs) have become the third largest air pollutants, following particulates and sulfur dioxide. VOCs in the atmosphere have toxic or mutagenic impacts on human life and organisms, and lead to secondary pollution because of forming photochemical fog with nitrogen oxide under certain conditions. Because the components of VOCs in the atmosphere are complex and their concentration is very low, the monitoring of VOCs in ambient air has been paid substantial attention.<sup>1</sup> Solid adsorbents, including activated charcoal, graphitized carbon black, carbon molecular sieves and porous polymers, are frequently employed in the preconcentration of trace VOCs from environmental samples, due to their capabilities for enrichment, convenience of use, and cost-effectiveness.<sup>2,3</sup> The selection of adsorbents is therefore important and directly related to the accuracy and precision of determination.

The ideal adsorbents should be chemically inert, thermally stable, low background, quantitative adsorption and desorption both polar and nonpolar compounds, uninfluenced by the humidity of the air.<sup>4-7</sup> Furthermore, other factors, including life-span, mechanical intensity and convenience should also be taken into account. Because each adsorbent has a different retention property for VOCs, a kind of adsorbent can not be suitable for collecting all of the compounds with different volatility and polarity. The combination of various adsorbents can collect extensive VOCs to avoid any shortcoming of each adsorbent. Therefore, it is important to explore the new adsorbent and develop multi-layer adsorbents to establish simple and reliable

methods.

Multi-walled carbon nanotubes (MWCNTs) are a kind of new carbon-based nano-material that has attracted great attention in many application fields, such as scanning probe microscopy,<sup>8</sup> catalysis,<sup>9</sup> hydrogen storage media<sup>10</sup> and electrochemical sensors,<sup>11</sup> due to their unique mechanical intensity, porous structure, and large surface area. In particular, the potential of MWCNTs as solid-phase extraction (SPE) adsorbents for the preconcentration of environmental pollutants, such as trace metal ions,<sup>12</sup> chlorophenols (CPs),<sup>13</sup> volatile organic compounds (VOCs),<sup>14</sup> bisphenol A (BPA),<sup>15</sup> and phthalate esters (PAEs),<sup>16</sup> has been investigated in recent years.

The retention characteristics of MWCNTs were evaluated and the thermal desorption recoveries of 11 kinds of commercially available adsorbents were compared in the present work. A kind of new multi-layer adsorbents including Tenax TA/MWCNTs/Carboxen 564 was developed for collecting volatile organic compounds in ambient air. The target compounds used in the experiment were the representative compounds with latent toxicity, frequent appearance and high concentration in the atmosphere. Compared with single MWCNTs or Tenax TA sampling tubes, the adsorption and desorption efficiencies were improved by using the multi-layer adsorbents, Tenax TA/MWCNTs/Carboxen 564. New multi-layer adsorbents were successfully applied to the determination of VOCs in ambient air.

## Experimental

### *Chemicals and reagents*

Standard solutions of TVOCs (benzene, toluene, butyl acetate, ethylbenzene, *o*-xylene, *m*-xylene, styrene, *p*-xylene and *n*-undecane) were obtained from Institute for Reference Materials of State Environmental Protection Administration of China;

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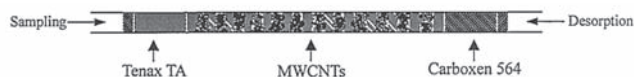


Fig. 1 Loading of the sampling tubes.

each solution was  $1000 \mu\text{g mL}^{-1}$ , respectively. All reagents and solvents used were of analytical reagent grade, or better.

A gas standard was prepared by injecting  $2 \mu\text{L}$  of the  $1000 \mu\text{g/mL}$  VOCs standard solution into a sampling bag (HuaYuan Inc., PRC) filled with 2 L nitrogen ( $\geq 99.999\%$ ) as the dilution gas. Gas standards were prepared with a relative humidity of  $65 \pm 5\%$  and room temperature.

The MWCNTs studied in this experiment were prepared by Tsinghua University by catalytic cracking a mixture gas of propylene and hydrogen ( $\text{C}_3\text{H}_6/\text{H}_2$ ). The specific areas of MWCNTs, determined by ASAP 2000 (Micromeritics, GA, USA), were  $111.3 \text{ m}^2 \text{ g}^{-1}$ , and the pore diameters were approximately  $200 \text{ \AA}$ .

#### Preparation of sampling tubes

Sampling tubes made of glass ( $16 \text{ cm} \times 4 \text{ mm}$  i.d. and a wall thickness of  $2 \text{ mm}$ ) were rinsed by deionized water and methanol, respectively. Figure 1 is a sketch of the loading of the sampling tubes;  $60 \text{ mg}$  of Tenax TA,  $20 \text{ mg}$  of MWCNTs,  $120 \text{ mg}$  of Carboxen 564, and a small amount of deactivated quartz wool (RHEODYNE, USA) were used by turns to improve the venting quality in each glass tube. Deactivated wire netting at both ends was applied to seal the adsorbents. All of the tubes were activated for  $2 \text{ h}$  by heating at  $350^\circ\text{C}$  in a stream of ultrapure nitrogen ( $\geq 99.999\%$ ) at a flow rate of  $100 \text{ mL min}^{-1}$  before use. After turning off the heater, the sampling tubes were purged continuously by  $\text{N}_2$  until the tubes cooled to room temperature. Before and after sampling, all tubes were plugged tightly by special Teflon screw caps and stored in a clean desiccator at room temperature.

#### The adsorption and desorption procedure

The sampling bag, the sampling tube and air sampling pump (CD-2A, Beijing, PRC) were connected by silicone tubes. The sampling was done by an air-sampling pump at room temperature. The desorption gases were collected by a  $100 \text{ mL}$  syringe, and then extracted by a SPME device (Supelco, USA). After extraction, VOCs were analyzed by gas chromatography-flame ionization detector (GC-FID) (Finnigan, Thermo, USA).

#### GC-MS/FID conditions

The determination was carried out by gas chromatograph (GC) (Finnigan TRACE GC 2000, Thermo, USA) equipped with a flame ionization detector (FID). The separations of 9 compounds (benzene, toluene, butyl acetate, ethylbenzene, *o*-xylene, *m*-xylene, styrene, *p*-xylene, *n*-undecane) were performed with an Agilent PONA capillary column ( $50 \text{ m} \times 0.2 \text{ mm}$  i.d.,  $0.5 \mu\text{m}$  film thickness), and the chromatographic peaks were identified by mass spectrometry (MS) (TRACE DSQ, Thermo, USA). The GC-MS/FID conditions used in the experiments were as follows: The carrier gases of GC-FID and GC-MS were nitrogen ( $99.999\%$ ) and helium ( $99.996\%$ ), respectively, at a flow-rate of  $0.9 \text{ mL min}^{-1}$ . The injection port was maintained at  $220^\circ\text{C}$ , with a 15:1 split ratio. The temperature of FID was kept at  $250^\circ\text{C}$ . The flame was supported by a mixture of  $\text{H}_2$  at  $30 \text{ mL min}^{-1}$ , air at  $300 \text{ mL min}^{-1}$ , and  $\text{N}_2$  at  $40 \text{ mL min}^{-1}$ . An initial oven temperature of  $40^\circ\text{C}$  for  $20 \text{ min}$  was adopted, and then increased to  $200^\circ\text{C}$  at a

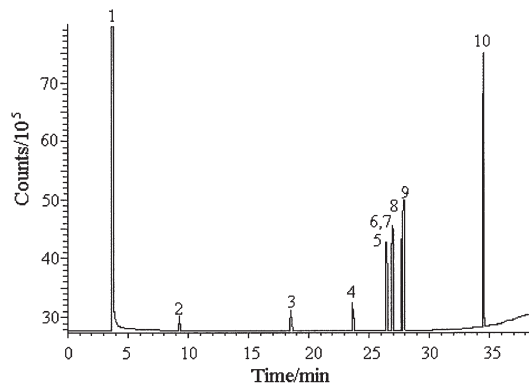


Fig. 2 Chromatogram of 9 volatile organic compounds. 1, Methanol; 2, benzene; 3, toluene; 4, butyl acetate; 5, ethylbenzene; 6, 7, *p*-xylene, *m*-xylene; 8, styrene; 9, *o*-xylene; 10, *n*-undecane.

rate of  $8^\circ\text{C min}^{-1}$ . The transfer line between GC and MS was kept at  $250^\circ\text{C}$ . The mass spectrometer was scanned from  $m/z$  50 to 600. The temperature of the EI source was kept at  $250^\circ\text{C}$ . The electronic energy was  $70 \text{ eV}$ . The FID chromatogram of the compounds is presented in Fig. 2.

## Results and Discussion

#### Breakthrough characteristics of MWCNTs

The breakthrough volume (BTv) or breakthrough capacity (BTC) of adsorbents is an important parameter for evaluating the properties of the adsorbents. It is closely related to the types of adsorbents, the sampling velocity, the temperature of adsorption, and the kinds of VOCs. The safe sampling volume (SSV) or safe sampling capacity (SSC) of adsorbents can be estimated according to the breakthrough volumes or breakthrough capacity of the adsorbents.

BTv of MWCNTs for the sampling of VOCs were estimated by connecting the MWCNTs sampling tube and the Tenax TA sampling tube in series with a silicone tube; a  $10 \mu\text{g L}^{-1}$  standard mixture gas was passed through the two sampling tubes at a flow-rate of  $0.1 \text{ L/min}$ . The effluents of the MWCNTs sampling tube and the Tenax TA sampling tube were measuring by the peak of each compound at certain intervals. The breakthrough volume of MWCNTs was defined as the volume at which 10% of the total sampling amount of each compound appeared in the Tenax TA sampling tube. The safe sampling volume (SSV) is calculated by  $V_{\text{max}} = (V_b \times m)/1.5$ , where  $V_{\text{max}}$  is the safe sampling volume (L),  $V_b$  is the BTv (L/g) of the compound tested and  $m$  is the amount (g) of adsorbent in the sampling tube; 1.5 is a safe coefficient for calculating SSV under a variable sampling environment condition, which is suitable at environment temperature of  $25 - 30^\circ\text{C}$ .

Table 1 summarizes the breakthrough volumes, breakthrough capacity, safe sampling volume and safe sampling capacity for each compound when the amount of adsorbent was  $50 \text{ mg}$ , and the concentration of the tested compound was  $10 \mu\text{g L}^{-1}$  for each compound. From Table 1, the results showed that the breakthrough volume and the safe sampling volume of MWCNTs sampling tube was about  $10 - 70 \text{ L g}^{-1}$ ; The breakthrough capacity and the safe sampling capacity were about  $100 - 700 \mu\text{g g}^{-1}$ . The breakthrough characteristics of the MWCNTs sampling tube were excellent, so that MWCNTs as the material in the air sampling became possible.

Table 1 Breakthrough characteristics of MWCNTs

Compound	Breakthrough		Safe sampling	
	Volume (BTV) <sup>a</sup> / L g <sup>-1</sup>	Capacity (BTC) <sup>a</sup> / μg g <sup>-1</sup>	Volume (SSV) <sup>a</sup> / L g <sup>-1</sup>	Capacity (SSC) <sup>a</sup> / μg g <sup>-1</sup>
1,2-Dichloroethane	22 ± 3	220 ± 30	15 ± 3	150 ± 30
Benzene	21 ± 4	210 ± 40	14 ± 3	140 ± 30
Toluene	37 ± 3	370 ± 30	25 ± 3	250 ± 30
<i>n</i> -Heptane	23 ± 3	230 ± 30	15 ± 3	150 ± 30
Ethylbenzene	51 ± 4	510 ± 40	34 ± 4	340 ± 40
<i>p</i> -Xylene	16 ± 3	160 ± 30	11 ± 3	110 ± 30
<i>m</i> -Xylene	17 ± 4	170 ± 40	11 ± 4	110 ± 40
Styrene	69 ± 4	690 ± 40	46 ± 3	460 ± 30
<i>o</i> -Xylene	15 ± 3	150 ± 30	10 ± 3	100 ± 30

a. BTV was the volume when the concentration of compound collected was 10 μg L<sup>-1</sup>.

#### The selection of the adsorbents

The recovery of thermal desorption is considered to be an important factor to reveal the degree of irreversible adsorption for the adsorbent at a certain desorption temperature in order to evaluate the property of the adsorbent for the sampling and analysis of VOCs in ambient air. Eleven kinds of adsorbents (including Activated charcoal, Tenax TA, Carboxen 564, Chromosorb 101, Chromosorb 102, Chromosorb 103, Chromosorb 105, Porapak Q, GDX 301, XAD-2, and MWCNTs) were compared; the adsorption and desorption efficiencies of Tenax TA, Carboxen 564, and MWCNTs for the test compounds are given in Table 2.

The results showed that the adsorption and desorption efficiencies of MWCNTs were satisfied for compounds with a low boiling point, such as *n*-pentane, *n*-hexane, benzene and ethyl acetate, but the desorption efficiencies were relatively low for compounds with a high boiling point, such as *n*-decane, *n*-undecane, and styrene. Tenax TA has a relatively low surface area (about 15 m<sup>2</sup> g<sup>-1</sup>), but its low background and high-temperature stability allows for the recovery of many semi-volatile molecules, which makes it a very useful adsorbent for collecting compounds from atmospheres of low concentrations. Carboxen 564 with a high porosity is relatively hydrophobic, so that it provides enhanced storage stability for reactive compounds, but is not sufficiently inert at high temperatures.<sup>17</sup> By combining the advantages of three adsorbents, a new multi-layer adsorbents was developed using Tenax TA/MWCNTs/Carboxen 564. The recoveries of the multi-layer adsorbents shown in Table 1 were higher as a whole than those of single Tenax TA, MWCNTs, and Carboxen 564, especially for *n*-undecane, styrene and tetrachloromethane.

#### Activation and regeneration

The activation and regeneration of the Tenax TA/MWCNTs/Carboxen 564 sampling tubes were investigated. The results showed that sampling tubes were kept at 300°C for 90 min using nitrogen (≥ 99.999%) at a flow-rate of 100 mL min<sup>-1</sup> before use would obtain a low background. The background disturbances in the chromatograms were caused by the breakdown of Tenax TA. The sampling tubes of multi-layer adsorbents did not have severe background disturbances when they were used to adsorb and desorb VOCs. A regeneration test also showed that the sampling tubes of multi-layer adsorbents kept for 15 min at 300°C using nitrogen (≥ 99.999%) at a flow-rate of 20 mL min<sup>-1</sup> would be of low background after use.

Table 2 Recoveries (%) of adsorption and desorption for tested compounds<sup>a</sup>

Compound	MWCNT	Tenax TA	Carboxen 564	Tenax TA/ MWCNT/ Carboxen 564
Alkane				
<i>n</i> -Pentane	96 ± 3 <sup>b</sup>	10 ± 5	84 ± 3	95 ± 3
Cyclohexane	98 ± 2	34 ± 4	80 ± 3	97 ± 2
<i>n</i> -Hexane	95 ± 2	93 ± 2	75 ± 4	95 ± 2
<i>n</i> -Heptane	98 ± 2	94 ± 3	78 ± 3	95 ± 3
<i>n</i> -Octane	94 ± 2	95 ± 2	80 ± 2	99 ± 2
<i>n</i> -Nonane	90 ± 3	95 ± 2	75 ± 3	94 ± 2
<i>n</i> -Decane	74 ± 4	90 ± 4	71 ± 2	96 ± 2
<i>n</i> -Undecane	38 ± 5	90 ± 2	66 ± 4	88 ± 3
Aromatic hydrocarbon				
Benzene	90 ± 2	90 ± 3	60 ± 4	91 ± 2
Toluene	90 ± 3	90 ± 2	67 ± 2	92 ± 2
Ethylbenzene	101 ± 2	85 ± 3	70 ± 2	90 ± 3
<i>p</i> -Xylene	99 ± 2	97 ± 2	72 ± 3	95 ± 2
<i>m</i> -Xylene	87 ± 4	90 ± 2	72 ± 3	91 ± 2
Styrene	77 ± 3	90 ± 2	79 ± 2	90 ± 3
<i>o</i> -Xylene	89 ± 2	94 ± 2	81 ± 2	91 ± 2
Halogenated hydrocarbon				
Dichloromethane	85 ± 3	6 ± 5	51 ± 4	83 ± 4
Trichloromethane	97 ± 2	21 ± 5	49 ± 3	95 ± 2
1,2-Dichloroethane	103 ± 2	44 ± 3	79 ± 3	101 ± 2
Tetrachloromethane	65 ± 4	34 ± 4	59 ± 2	70 ± 3
Alcohol				
2-Propanol	90 ± 3	38 ± 5	83 ± 2	90 ± 3
1-Butanol	95 ± 2	61 ± 4	85 ± 2	96 ± 2
1-Pentanol	94 ± 2	65 ± 2	82 ± 3	100 ± 2
Ester				
Ethyl acetate	100 ± 2	30 ± 4	70 ± 4	98 ± 2
Butyl acetate	98 ± 2	87 ± 2	70 ± 2	99 ± 2
Isoamyl acetate	94 ± 3	82 ± 3	65 ± 3	90 ± 4

a. The sampling tubes were all packed with the same amount of adsorbent (150 mg) except MWCNTs (50 mg).

b. *n* = 5.

#### Water adsorption

In the sampling of VOCs, the effect of water must be taken into account. The retention of VOC on adsorbents will be changed and the safe sampling volume of the adsorbent is reduced when water exists. In addition, difficulties will also be caused in the separation of the GC column, and even irreversible damage is caused to the capillary column. In order to simulate the humidity in air, the dilution gas, N<sub>2</sub>, was passed through deionized water (relative humidity, 56%) before filling the sampling bag when the gas standard was prepared. The recoveries of the compounds under this moisture condition were determined, and the results are given in Fig. 3.

The results showed that the recoveries, retention times and peaks of 9 kinds of VOCs did not change remarkably, and negative peaks did not exist on the chromatogram when the Tenax TA/MWCNTs/Carboxen 564 was used as multi-layer adsorbents. Although a large specific area generally results in a strong adsorption property for water, MWCNTs has a particular hydrophobicity because of hydrophobic and nonpolar surfaces containing an analog-graphite hexatomic ring structure. The hydrophobicity of the sampling tube can avoid a reduction of the recovery, and simplifies the sampling device and the experimental procedure.

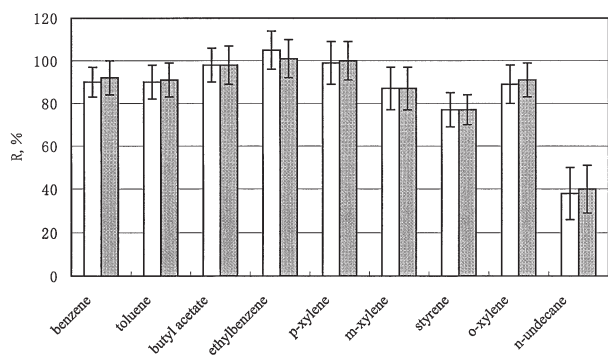


Fig. 3 Effect of water for adsorption-desorption efficiencies. □, H<sub>2</sub>O < 5 ppm (high purity nitrogen, the water is less than 5 ppm); ■, pass through the water, relative humidity is 56%.

Table 3 Ratios of the requirement of DP and DVP for the sampling tube

Compound	DP, % for MWCNTs	DP, % for Tenax TA/MWCNTs/Carboxen 564	DVP, % for MWCNTs	DVP, % for Tenax TA/MWCNTs/Carboxen 564
Benzene	71.4	85.7	85.7	85.7
Toluene	85.7	85.7	85.7	85.7
Butyl acetate	85.7	85.7	85.7	85.7
Ethylbenzene	100	100	100	100
<i>p</i> -Xylene	100	100	100	100
<i>m</i> -Xylene	85.7	85.7	85.7	85.7
Styrene	100	100	100	100
<i>o</i> -Xylene	100	100	100	100
<i>n</i> -Undecane	57.1	85.7	57.1	71.4

Table 4 VOCs (mg/m<sup>3</sup>) in air using Tenax TA/MWCNTs/Carboxen 564<sup>a</sup>

Compound	Sample 1		Sample 2		Sample 3	
	A	B	A	B	A	B
Benzene	ND	ND	ND	0.075 ± 0.002	ND	ND
Toluene	ND	ND	ND	0.068 ± 0.001	ND	0.069 ± 0.002
Butyl acetate	0.121 ± 0.003	0.130 ± 0.002	0.112 ± 0.003	0.125 ± 0.003	0.166 ± 0.002	0.180 ± 0.002
Ethylbenzene	0.126 ± 0.003	0.130 ± 0.002	0.121 ± 0.003	0.130 ± 0.002	0.135 ± 0.002	0.148 ± 0.002
<i>p,m</i> -Xylene	0.114 ± 0.004	0.119 ± 0.002	0.103 ± 0.003	0.113 ± 0.003	0.136 ± 0.003	0.145 ± 0.002
Styrene	0.012 ± 0.001	0.016 ± 0.001	0.015 ± 0.002	0.016 ± 0.001	0.012 ± 0.002	0.011 ± 0.002
<i>o</i> -Xylene	0.124 ± 0.003	0.131 ± 0.003	0.125 ± 0.003	0.128 ± 0.002	0.108 ± 0.004	0.121 ± 0.003
<i>n</i> -Undecane	0.013 ± 0.002	0.016 ± 0.002	0.008 ± 0.001	0.010 ± 0.001	0.005 ± 0.002	0.006 ± 0.002

Compound	Sample 4		Sample 5	
	A	B	A	B
Benzene	ND	0.069 ± 0.002	ND	0.072 ± 0.003
Toluene	ND	ND	ND	0.058 ± 0.003
Butyl acetate	0.174 ± 0.002	0.181 ± 0.002	0.158 ± 0.003	0.169 ± 0.002
Ethylbenzene	0.118 ± 0.002	0.122 ± 0.002	0.107 ± 0.002	0.116 ± 0.002
<i>p,m</i> -Xylene	0.141 ± 0.004	0.150 ± 0.002	0.127 ± 0.002	0.141 ± 0.003
Styrene	0.020 ± 0.002	0.023 ± 0.002	0.025 ± 0.002	0.028 ± 0.002
<i>o</i> -Xylene	0.137 ± 0.002	0.139 ± 0.002	0.143 ± 0.002	0.150 ± 0.002
<i>n</i> -Undecane	0.005 ± 0.002	0.005 ± 0.002	0.007 ± 0.001	0.007 ± 0.002

A, Tenax TA; B, Tenax TA/MWCNTs/Carboxen 564; ND, not detection. a. *n* = 5.

#### Sampling reproducibility

The reproducibility of adsorbent tubes depends on many factors, such as the quality and pretreatment of the sampling tube, the storage condition, the sampling procedure and the analysis condition. The reproducibility of the MWCNTs and Tenax TA/MWCNTs/Carboxen 564 adsorbents tube was estimated by duplicate precision (DP) and distributed volume pair (DVP) on the basis of the EPA TO-17 criteria.

Table 3 gives the ratios of the requirement of DP for all tested compounds, ranging from 85.7 to 100%, and DVP ranging from 71.4 to 100%. However, the multi-layer adsorbents, Tenax TA/MWCNTs/Carboxen 564, obviously improved the sampling reproducibility for compounds with high volatility and large molecular weight, such as *n*-undecane. Its ratios of the requirement of DP changed from 57.1 (for MWCNTs) to 85.7 (for Tenax TA/MWCNTs/Carboxen 564) and DVP changed from 57.1 (for MWCNTs) to 71.4 (for Tenax TA/MWCNTs/Carboxen 564).

#### Air sample analysis

Samples in indoor air were collected in the laboratory. The sampling and analysis were performed according to national standard GB/T 18883-2002 of indoor air (China), including its Appendix A, B and C. The room was closed for more than 8 h before sampling. The sampling location should be far from the ventilator and the distance to the wall kept at more than 0.5 m. The height of the sampling tube was 1.5 m from the ground, the height of the physical breath; 30 L of air was collected simultaneously by multi-layer adsorbents and Tenax TA at a rate of 0.5 L min<sup>-1</sup>.

For monitoring ambient or relatively unpolluted indoor air, the sampling reliability of Tenax TA has been proved.<sup>18</sup> For estimating the accuracy of the new multi-layer adsorbent, the concentrations of tested VOCs collected by the multi-layer adsorbents and Tenax TA were compared; the results are given in Table 4. As can be seen, the concentrations of VOCs including benzene, toluene, butyl acetate, ethylbenzene; *p*-, *m*-xylene, styrene, *o*-xylene, and *n*-undecane, obtained with the



multi-layer adsorbents, are in good agreement with the results of Tenax TA as the adsorbent. Furthermore, the compounds with a low boiling point, such as benzene and toluene can be measured when the multi-layer adsorbents were used. Therefore, it is clear that the combined adsorbents can be applied to analyze VOCs in ambient air with a reliable accuracy and sensitivity.

## Conclusions

A kind of new multi-layer adsorbents including Tenax TA/MWCNTs/Carboxen 564 was developed for collecting volatile organic compounds in ambient air. The recoveries of multi-layer adsorbents were higher as a whole than those of single Tenax TA, MWCNTs, and Carboxen 564, especially for *n*-undecane, styrene and tetrachloromethane. The hydrophobicity of the sampling tube can avoid a reduction of the recovery and simplify the sampling device and the experimental procedure. The sampling reproducibility including compounds with high volatility and large molecular weight was improved by using multi-layer adsorbents, Tenax TA/MWCNTs/Carboxen 564.

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