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Evaluation of multi-walled carbon nanotubes as an adsorbent for trapping volatile organic compounds from environmental samples

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Abstract

A type of purified multi-walled carbon nanotubes (PMWCNTs) prepared by catalytic decomposition of methane, with a surface area of $98\,m^2/g$, was evaluated as an adsorbent used for tapping volatile organic compounds (VOCs). The performance in evaluation was based on breakthrough volumes (BTVs) and recoveries of selected VOCs. PMWCNTs were also used as a trap packing material to adsorb VOCs purged from spiked water sample. Due to their porous structure, PMWCNTs were found to have much higher BTVs than that of Carbopack B, a graphitized carbon black with the same surface area as PMWCNTs. The recoveries of the tested VOCs trapped on PMWCNTs ranged from 80 to 110%, and not affected by the humidity of purge gas. The results indicate that PMWCNTs are a potential useful adsorbent for direct trapping VOCs from air samples and may be a supplement to VOCARB 3000, a commercially available trap, in purge-and-trap system to preconcentrate VOCs from water samples.
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1. Introduction

Monitoring of volatile organic compounds (VOCs) in ambient air and water sample is an important analytical task because of VOCs' great contribution to environmental pollution and their potential threat to human health. One of the most convenient and widely employed ways to monitor VOCs in ambient air is the use of a solid adsorbent for the trapping of VOCs [1–4]. The VOCs adsorbed on the adsorbent can be desorbed by the methods of thermal desorption or solvent extraction, and then analyzed with gas chromatography (GC) or gas chromatography-mass spectrometer (GC/MS) [5]. The standard method for monitoring water sample for VOCs is purge-and-trap method [6–8]. VOCs are purged by a continuous flow of inert gas through the water sample and adsorbed onto a solid adsorbent, and then thermally desorbed into a gas chromatographic column for separation and detection.

Solid adsorbents, including activated charcoal, graphitized carbon black, carbon molecular sieves and porous polymers, are frequently employed in preconcentration of trace VOCs from environmental samples [9–11]. Among those as a popular adsorbing material, carbonaceous adsorbents have long been used. Since each type of adsorbents has different retention capacities for VOCs, the selection of adsorbent is therefore important, which is based on their adsorbent properties, e.g. the breakthrough volume (BTV) of a compound on a specific adsorbent and the recovery of the compound from it have been usually investigated to evaluate the adsorbent characteristics [12–16]. No adsorbent can solve all the problems in VOCs analysis. For example, activated charcoal is cheaper and has high BTV, but high background and low recovery may not be avoided while it is applied in VOCs analysis [9]. Therefore, tremendous effort has been made in recent years to seek new adsorbents for preconcentrating VOCs from environmental samples [12–16].

Since its discovery in 1991 [17], carbon nanotubes (CNTs) have attracted great attention because of their unique properties. CNTs can be visualized as a sheet of graphite that has been rolled into a tube, with either single walled or multi-walled structures. Currently, large-scale preparation of

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CNTs has been realized [18]. To bring a way out to the application of CNTs is getting more and more urgent. Due to the porous graphite structure of CNTs, it is possible to use CNTs as adsorbent in preconcentrating VOCs from environmental samples.

The objective of this study is to investigate the properties of CNTs and the possibilities of their applications in environmental analysis. To achieve the aims, a kind of purified multi-walled CNTs (PMWCNTs) was evaluated as an adsorbent in trapping VOCs in gaseous samples and indirectly from water samples. First, BTVs of selected VOCs on PMWCNTs were determined by gas chromatography and compared with those on graphitized carbon black (Carbopack B). Second, a Purge-and-trap system coupling with GC was applied to determine the recoveries of VOCs on PMWCNTs, Carbopack B and the multi-bed adsorbent in VOCARB 3000. The effect of purge gas humidity on recoveries was also investigated. Finally, PMWCNTs was applied as a trap packing material in purge-and-trap system to enrich VOCs from water samples.

2. Experimental

2.1. Material

Benzene, toluene, p-xylene, o-xylene, ethyl benzene, n-pentane, n-hexane, cyclohexane, n-heptane, dichloromethane, trichloromethane, tetrachioromethane, 1,2-dichloroethane, acetone, ether, ethyl acetate, n-propanol, n-butanol, all of analytical grade, were purchased from Shanghai Chemical Co. (Shanghai, China). VOCARB 3000, which is a commercially available multi-bed trap of the combination of Carbopack B, Carboxen 1000 and Carboxen 1001, and Carbopack B (60–80 mesh, surface area $100 \, m^2/g$) were purchased from Supelco Co. (Bellefonte, PA, USA). Multi-walled carbon nanotubes (MWCNTs) were kindly provided by Department of Chemistry, Xiamen University (Xiamen, China). The MWCNTs, with o.d. of 15–30 nm and i.d. of 3 nm, were prepared as follows: 12 mg of Ni-MgO catalyst precursor were packed into a quartz tube of 5 mm i.d., followed by heating the sample in a flow of purified H_2 from room temperature to 873 K and keeping it at the same temperature for a few minutes, and then introducing CH_4 with the flow-rate at 2.0 l/h. After 30 min of reaction, about 70 mg of raw MWCNTs were obtained [19]. They were further treated with H_2 stream of 10 ml/min under high temperature of 900 °C for 24 h, refluxed with 6 mol/l hydrochloric acid for 24 h, and then washed with distilled water to clean up the catalyst residual. The treatment procedures could limit the amount of hydrophilic functional groups on the surface and open the ends of the tubes, The surface area of the purified MWCNTs (PMWCNTs) was determined as $98 \, m^2/g$ by BET method. And particles ranging from 60 to 80 mesh were selected for this study.

2.2. Gas chromatographic measurement of BTVs

The BTV was determined with gas chromatography. The gas standard of individual VOC was prepared by injecting 0.5 μl of liquid chemical into a 100 ml vial sealed with a silicon rubber cap and filled with nitrogen. The vial was allowed to stand till the liquid chemical inside fully evaporated. Fifty microliter of the gas standard was injected into the gas chromatography with a syringe. A GC-9A gas chromatograph (Shimadzu Co, Kyoto, Japan) equipped with a flame ionization detector was applied to determine the retention volume of each 16 VOCs on the glass column (50 cm × 3 mm i.d.) packed with 0.3 g PMWCNTs and Carbopack B, respectively. The injection port and detector temperatures were both set at 250 °C. The flow rate of carrier gas N_2 was 48 ml/min. BTVs were calculated as the retention volume at 20 °C extrapolated from the plot of $\log V_g$ versus $1/T$ [12,20,21], where V_g was retention volume in liter at the designed oven temperature T in K. Triple determinations were performed for each compound at four different GC oven temperatures ranging from 40 to 320 °C, and the average was calculated. VOCARB 3000 is a multi-bed adsorbent tube, which contains three types of adsorbents, namely, Carbopack B, Carboxen 1000 and Carboxen 1001. The comparison of BTVs between a single adsorbent and a multi-bed adsorbent is not appropriate and not necessary for the evaluation of a new adsorbent. Therefore, the BTVs of VOCARB 3000 were not measured in the study.

2.3. Measurement of recoveries

The recovery of a specific compound was defined as the ratio of its GC signal peak area recorded from adsorption–desorption to that from a direct injection. Two stainless steel tubes (28.5 cm × 2.5 mm i.d.) packed with 0.65 g PMWCNTs and 0.45 g Carbopack B, respectively, and a commercial VOCARB 3000 trap were used as traps. An ENCON purge-and-trap system (EST Co., OH, USA) was coupled to a CP3800 gas chromatography (Varian Co., CA, USA) equipped with a flame ionization detector. The injection port and detector temperatures were both set at 250 °C. The flow rate of carrier gas N_2 was 10 ml/min. Splitless injection model was selected and a DB-624 column (70 m × 0.53 mm, $d_f = 3 \mu m$, J&W Scientific, CA, USA) was adopted. The column temperature was kept at 45 °C for 4.5 min, then increased to 110 °C at a rate of 10 °C/min, then increased to 160 °C at a rate of 25 °C/min and maintained for 1.5 min.

The gas standard of VOC mixtures was prepared by injecting 0.5 μl of each 16 VOCs into a 100 ml vial sealed with a silicon rubber cap and filled with nitrogen. The vial was allowed to stand till the liquid chemical inside fully evaporated. The stock solution of VOCs was prepared by adding 1 μl of each 10 liquid non-polar chemicals into a vial filled with 10 ml methanol.
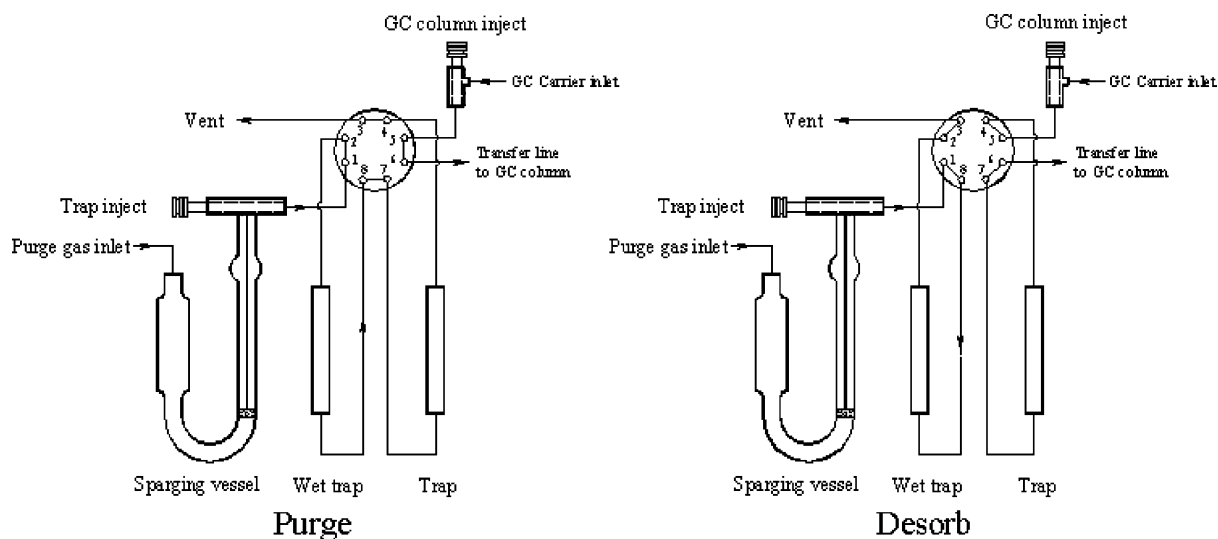
Fig. 1. The gas flow diagram of Purge and Desorb modes in ENCON purge-and-trap system.

Fig. 1 shows the gas flow diagram of ENCON purge-and-trap system in purge and desorps modes. ENCON has two injection ports, namely "trap inject" and "GC column inject", thus has two injection methods, namely, "trap injection method" and "column injection method". In the trap injection method, at first ENCON was set at purge mode, the temperature of trap was 35 °C, and the flow rate of purge gas N_2 was 40 ml/min. Fifty microliter of gas standard was injected into the system from the trap inject port, and the compounds were purged into the trap by purge gas and then adsorbed by the adsorbent in the trap. The purge step had been kept for 11 min, when ENCON was switched to desorb mode. While the trap temperature was quickly increased to 250 °C, the compounds were desorbed from the trap and transferred through a transfer line of temperature 200 °C to GC system for separation and detection. In this case, purge gas entered the sparging vessel directly and thus the humidity was 0%. During the process 440 ml purge gas passed through the trap. The compounds entered the GC system were considered as those recovered from the process of adsorption–desorption. Then ENCON ran the column injection method to obtain the data of direct injection. At the purge mode 50 μl of gas standard was injected into the GC system directly from column inject port without going through the trap. The recoveries were calculated from the signal peak areas of these two injection methods.

To use PMWCNTs as adsorbent in practical air sampling, consideration of sample gas humidity must be taken. In the above process of purge and trap, the purge gas humidity was 0%. In order to examine the effect of humidity on the adsorption and desorption, a wetted purge flow was designed to provide moisture condition. The original wet trap in EN-CON system was replaced with an empty stainless steel tube to avoid the removal of purge gas moisture. When the system was in purge mode, the sparging vessel was disconnected from the trap inject, then a humidity meter was inserted into

the sparging vessel to measure the humidity of the purging gas. Five milliliter VOCs-free water was added into the sparging vessel. Thus, the purge gas was wetted, while it passed the vessel, with the humidity of 70%. The recoveries of the compounds under this moisture condition were also determined.

2.4. Application of traps in preconcentration of VOCs in water samples

In order to compare the properties of PMWCNTs with other trap packing materials for the adsorption of VOCs from water sample, the following experiment was performed. Five milli1iter VOCs-free water, spiked with 1 μl of the stock solution of VOCs (20 μg/l for each compound), was analyzed with the purge-and-trap-GC system with the traps of PMWCNTs, Carbopack B and VOCARB 3000, respectively. The analytical procedure was the same as that described in Section 2.3 except water sample was applied in the trap injection method and 1 μl of the stock solution of VOCs was used in the column injection method. The recoveries of the compounds were calculated.

3. Results and discussion

3.1. BTVs of compounds for PMWCNTs and Carbopack B

BTVs of the tested VOCs, namely benzene, toluene, ethylbenzene, p-xylene, n-pentane, cyclohexane, n-hexane, n-heptane, dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane, acetone, ether, ethyl acetate, and n-propanol, were listed in Table 1. Even though the condition of designed experiments were not exactly the same as those of real air sampling, the calculated BTVs

Table 1
BTVs (l/g, 20 °C) of tested compounds on Carbopack B and MWCNTs, respectively

Compounds	Aromatic hydrocarbons				Alkanes			
	Benzene	Toluene	Ethylbenzene	*p*-Xylene	*n*-Pentane	Cyclohexane	*n*-Hexane	*n*-Heptane
Carbopack B	3.72×10^2	1.34×10^4	2.10×10^4	3.23×10^5	5.20×10^1	6.10×10^1	1.37×10^3	3.11×10^4
MWCNTs	7.96×10^4	5.24×10^6	7.73×10^7	4.75×10^8	5.33×10^3	6.13×10^3	2.93×10^5	2.03×10^7
	Halogenated hydrocarbons				Other compounds			
	Dichloromethane	Trichloromethane	Tetrachloromethane	1,2-Dichloroethane	Acetone	Ether	Ethyl acetate	*n*-Propanol
Carbopack B	3.60×10^{-1}	6.70×10^0	2.85×10^1	1.30×10^1	8.70×10^{-1}	5.10×10^0	5.00×10^1	1.30×10^0
MWCNTs	1.74×10^1	3.70×10^2	1.16×10^3	1.19×10^3	5.89×10^1	9.55×10^2	4.84×10^3	1.39×10^2

provided useful information for theoretical evaluation. From the results it could be found that compounds with low boiling point such as dichloromethane and polar functional groups such as acetone and *n*-propanol had small BTVs on Carbopack B, indicating the weak retention of Carbopack B towards those compounds. On PMWCNTs, all the tested compounds presented two to three-orders larger BTVs than those on Carbopack B showing much stronger retention. It has been revealed that the chemically active atoms or irregularities such as pores on carbon surface can result in much higher BTVs [15]. The structure of PMWCNTs is open-ended, with adsorption sites on both internal and external surfaces. The open-ended carbon nanotubes exhibited a stronger binding energy and adsorption affinity towards compounds due to large internal surfaces [22,23]. On the other hand, Carbopack B possesses graphite structure of nonporous and planar surface, thus the lower binding energy and adsorption affinity [22,23]. Even though both adsorbents had the similar surface areas, PMWCNTs showed greater adsorption capacity than Carbopack B due to their porous structure. The BTVs of the tested VOCs on PMWCNTs were high enough so that the use of the material in air sampling might become possible.

3.2. Recoveries of the tested compounds

In most cases, to evaluate the properties of one adsorbent for air monitoring, thermal desorption recovery is considered as an important factor to reveal the degree of irreversible adsorption on the adsorbent at a certain desorption temperature. A compound in the trap injection method undertook the steps of adsorbing and thermal desorbing. All the compounds were expected to adsorb on the adsorbent if the breakthrough had not occurred. After heating the adsorbed compound was desorbed and then determined. The ratio of amount of detected to that of injected was defined as recovery and was considered as thermal desorption recovery in this study if there was no break through. Fig. 2 reports the chromatograms of tested compounds in trap injection method using VOCARB 3000, PMWCNTs and Carbopack B as traps, respectively, while the relative humidity of purge gas was 70%. The tested compounds included *n*-pantane, ether, acetone, dichloromethane, cyclohexane, *n*-propanol, ethyl acetate, trichloromethane,

n-hexane, benzene, *n*-heptane, *n*-butanol, toluene, ethyl benzene, *p*-xylene, and *o*-xylene. All the compounds except ethyl benzene and *p*-xylene were completely separated. A chromatogram of a blank run was also provided. A very low background signal from the blank run on PMWCNTs column had been observed.

Table 2 reports the recoveries of some compounds on Carbopack B, PMWCNTs and VOCARB 3000 with purge gas humidity of 0 and 70%, respectively. For Carbopack B, the recoveries of dichloromethane, acetone and *n*-propanol at humidity of 0%, were 0, 12 and 86%, respectively, while recoveries of other some compounds were over 90%. Since Carbopack B is known as non-specific adsorbent with homogenous surface [24], London dispersion is the driving force in the adsorption process. In addition, the degree of irreversible reaction of the compound on Carbopack B should be very small under the experimental condition. The low recoveries found for dichloromethane, acetone and *n*-propanol, were due to their low BTVs, which could be verified with the data in Table 1. As to PMWCNTs and VOCARB 3000, the recoveries of all tested compounds were near 100%. No breakthrough had occurred on those two adsorbents during adsorbing, and the adsorbed compounds desorbed completely during thermal desorbing. The results indicated that PMWCNTs possess homogenous surface, and for the compounds studied the irreversible reaction on PMWCNTs is very small. This could also be verified by the symmetric peaks of some polar compounds on the gas chromatographic column packed with PMWCNTs [25]. It is also noted that the recoveries of compounds with relatively higher boiling point such as ethyl benzene, *p*-xylene and *o*-xylene were relatively lower. This could be improved by increasing the desorbing temperature.

In practical air sampling, the effect of gas humidity should be taken into account. The surface of carbon adsorbents, such as activated charcoal and even graphitized carbon black with the most homogenous surface, can be modified by humidity [9,24]. The modification was considered to be due to the existence of polar function group on their surface. The competition for the adsorption sites between analyte and water molecules on the adsorbent will result in the decrease of BTVs [26], leading to an increase of breakthrough. For Carbopack B, when the purge gas humidity was increased
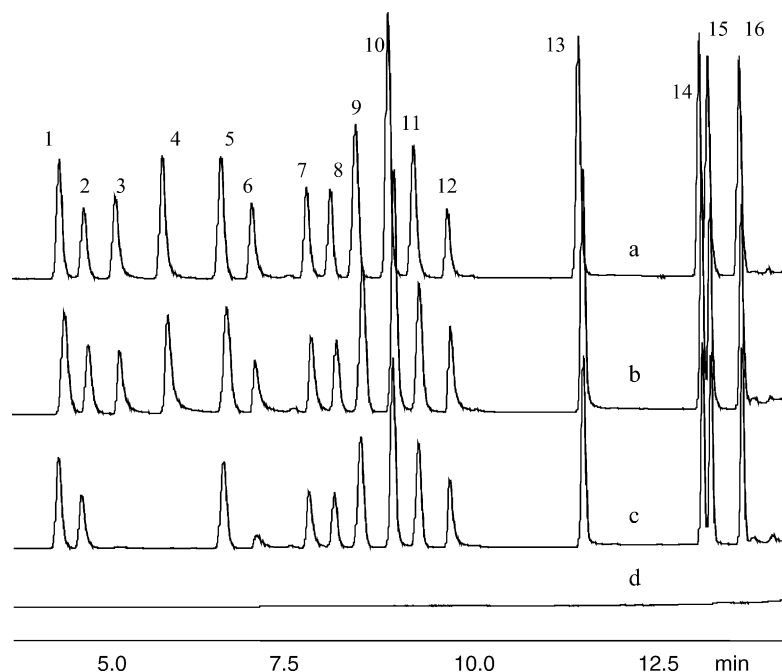
Fig. 2. Chromatograms of tested compounds of trap injection method using different traps with relative humidity of 70%: (a) Vocarb 3000, (b) PMWCNTs, (c) Carbopack B and (d) blanks on PMWCNTs. Peaks (1) *n*-pentane, (2) ether, (3) acetone, (4) dichloromethane, (5) cyclohexane, (6) *n*-propanol, (7) ethyl acetate, (8) trichloromethane, (9) *n*-hexane, (10) benzene, (11) *n*-heptane, (12) *n*-butanol, (13) toluene, (14) ethyl benzene, (15) *m*-xylene and (16) *o*-xylene.

from 0 to 70%, the recoveries of acetone and *n*-propanol decreased from 12 and 86 to 0 and 35%, respectively. On the other hand, the recoveries were not affected by gas humidity due to their high absorbing capacity in both PMWCNTs and VOCARB 3000. The results provide the possibility of PMWCNTs for further practical use as a trap in collecting analytes in air sample.

3.3. Application of traps for VOCs in water samples

Table 3 reports the recoveries of 10 non-polar compounds, dichloromethane, cyclohexane, trichloromethane, *n*-hexane, benzene, *n*-heptane, toluene, ethyl benzene *m*-xylene and *o*-xylene, in spiked water samples (20 μg/l for each compound) determined by a purge-and-trap system

Table 2
Recoveries (%) of tested compounds on Carbopack B, MWCNTs and VOCARB 3000 with humidity of 0 and 70%, respectively

Compounds	Carbopack B		MWCNTs		VOCARB 3000	
	0%	70%	0%	70%	0%	70%
n-Pantane	96 ± 2	103 ± 5	105 ± 5	107 ± 2	110 ± 3	103 ± 3
Ether	97 ± 3	111 ± 4	106 ± 5	107 ± 2	112 ± 3	109 ± 2
Acetone	12 ± 5	0	110 ± 4	107 ± 3	114 ± 2	109 ± 5
Dichloromethane	0	0	104 ± 4	105 ± 2	111 ± 2	109 ± 3
Cyclohexane	94 ± 4	100 ± 5	104 ± 5	108 ± 2	111 ± 3	99 ± 2
n-Propanol	86 ± 7	35 ± 22	100 ± 8	97 ± 6	106 ± 9	110 ± 5
Ethyl acetate	96 ± 4	98 ± 5	106 ± 7	105 ± 5	102 ± 3	109 ± 2
Trichloromethane	97 ± 3	98 ± 4	103 ± 4	104 ± 4	109 ± 2	100 ± 2
n-Hexane	98 ± 3	102 ± 5	105 ± 5	106 ± 5	112 ± 2	101 ± 2
Benzene	100 ± 4	105 ± 5	105 ± 5	107 ± 5	112 ± 2	105 ± 2
n-Heptane	98 ± 5	104 ± 4	103 ± 5	106 ± 5	112 ± 2	103 ± 2
n-Butanol	94 ± 3	112 ± 6	101 ± 7	106 ± 5	100 ± 6	111 ± 5
Toluene	100 ± 5	104 ± 4	103 ± 6	104 ± 6	110 ± 3	101 ± 4
Ethyl benzene	93 ± 2	92 ± 4	85 ± 8	88 ± 5	89 ± 5	93 ± 7
p-Xylene	92 ± 2	92 ± 3	86 ± 8	88 ± 6	90 ± 6	95 ± 7
o-Xylene	99 ± 2	94 ± 3	82 ± 8	86 ± 6	88 ± 6	93 ± 8

Desorption temperature 250 °C, *n* = 5.

Table 3
Recoveries (%) of the compounds from water samples using Carbopack B, PMWCNTs and VOCARB 3000 as trap, respectively

Compounds	Carbopack B	MWCNTs	VOCARB 3000
Dichloromethane	0	88 ± 7	92 ± 14
Cyclohexane	105 ± 6	110 ± 5	98 ± 11
Trichloromethane	98 ± 1	102 ± 5	105 ± 1
n-Hexane	97 ± 3	101 ± 71	99 ± 3
Benzene	107 ± 2	108 ± 5	111 ± 5
n-Heptane	106 ± 5	110 ± 9	99 ± 5
Toluene	101 ± 3	104 ± 4	108 ± 4
Ethyl benzene	98 ± 2	93 ± 4	96 ± 2
m-Xylene	97 ± 2	95 ± 5	96 ± 2
o-Xylene	100 ± 3	92 ± 4	94 ± 2

Desorption temperature 250 °C, $n = 5$.

using Carbopack B, PMWCNTs and VOCARB 3000 as traps, respectively. It can be seen that the recovery of dichloromethane was 0% when Carbopack B was used because of its lower BTV. However, the recoveries of others tested compounds were satisfied, which ranged from 98 to 105%. In contrast, all the tested compounds presented satisfactory recoveries (88–110%) when PMWCNTs and VOCARB 3000 were employed for trapping of tested compounds in water samples. The preliminary results showed that PMWCNTs could be a potential adsorbent as trap packing material in purge-and-trap system to adsorb VOCs from water samples because of its higher BTV. Further applications of PMWCNT to trap VOCs in various real waters are undergoing in this laboratory.

Nowadays MWCNTs have already been commercially produced on the kilogram to ton level [18]. The purification of MWCNTs is becoming simpler and easier with the various methods developing. One may expect that in the near future PMWCNTs can be commercial available with acceptable price. The application of PMWCNTS in VOCs analysis can be popular.

4. Conclusions

The adsorption property of PMWCNTs was studied and compared to those of Carbopack B and VOCARB 3000. The results indicated that because of the porous structure PMWCNTs had much higher BTVs than that of Carbopack B with the same surface area. The desorption recoveries of the tested compounds on PMWCNTs were all near 100%, and the irreversible adsorption of the tested compounds on PMWCNTs was neglected. On the basis of experimental results, it could be seen that PMWCNTs could be useful for trapping VOCs purged from water samples and direct preconcentrate VOCs in air samples.

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