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Original Article

Microtrapping of volatile organic compounds with carbon nanotubes

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Abstract

Micro-sorbent traps referred to as microtraps serve as integrated concentration-injection devices for continuous monitoring in gas phase streams. The application of carbon nanotubes as unique sorbents for the fabrication of microtraps for the nano-scale adsorption/desorption of volatile organic molecules is presented in this paper. The microtrap application requires high adsorption capacity as well as easy desorbability; the latter being critical for injection mode of these integrated devices. The micro-sorbent characteristics of single and multi-walled carbon nanotubes for gas phase adsorption/desorption of several volatile organic compounds like DCM, ethanol and benzene etc. has been studied. The nonporous nature of carbon nanotubes (CNTs) eliminates the mass transfer resistance related to diffusion into pore structures, thus allowing easy desorbability. At the same time, their high aspect ratios lead to large breakthrough volumes. As compared to a commercial sorbent carbopack^{TM}, the breakthrough volume was as much as an order of magnitude higher in the CNTs, while the higher rate of desorption measured as the peak width at half height of the desorption band was found nearly eight times lower (i.e., 0.26 seconds with SWNT and 1.89 seconds with carbopack^{TM}). The trapping and desorption characteristics of single and multi walled nanotubes were found to be comparable. We also found that the presence of disordered carbon impurities, which could be removed by controlled oxidative annealing, could greatly degrade the performance of CNTs. This research has suggested that CNTs can be used in micro-sorbent traps and surprisingly enhance the efficiency of the integrated concentration-injection devices. Consequently, this will open the doors to the application of high-capacity, CNTs-based sorbents as a better alternative to conventional sorbent in continuous monitoring devices.

Keywords: microtrap, continuous monitoring, volatile organic compounds, carbon nanotubes, sorbent

1. Introduction

The detection and quantitative measurement of volatile organic compounds (VOCs) at trace levels in air emissions is of considerable importance because they are hazardous to public health and cause ozone formation in the troposphere. The development of rapid and sensitive analytical instrumentation is necessary to monitor the ambient VOCs in the environment and to monitor emission sources. Traditional methods to analyze for VOCs in ambient air and stack emissions use either whole air samplers such as Tedlar bags and canisters or sorbent cartridges. In either case, the sample is collected in the field and the analysis is done in the laboratory. Consequently, there may be a significant delay between sampling and analysis. Also, there may be inaccuracies asso-

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ciated with sampling, sample transport and storage. Moreover, most of these techniques require extensive sample handling, which increases the analysis cost per sample (Brukh *et al.*, 2002 and Thammakhet *et al.*, 2005).

For process continuous environmental monitoring and process control, the analytical results are critical and the information is needed as soon as possible. Hence, there is a real need for instrumentation that can be used to carry out automated, on-line analysis to provide information on a continuous basis that can be used for process control and for meeting regulatory compliance. Gas chromatography (GC) is particularly attractive for monitoring VOCs because of its separation capability, with good sensitivity and selectivity (Mitra *et al.*, 1993 and Guo *et al.*, 1999).

Carbon nanotubes (CNTs) possess some highly desirable mechanical, thermal and electrical properties, which make them attractive for a wide range of applications ranging from field emission to reinforcements in nano-composites. Single-walled carbon nanotube (SWNT) and the multi-walled carbon nanotubes (MWNT) are formed by seamless rolling up of a single or multiple layers of graphene sheets respectively (Subramoney, 1998).

CNTs also have some excellent sorbent characteristics, which can be utilized in diverse applications. Studies have shown that CNTs can efficiently remove trace contaminants from air and water, and also trap small molecules such as H_2, O_2 and methane (Düren *et al.*, 2004 and Chen *et al.*, 2007). Their reported surface areas range between 150-3000 m^2/g, which makes them attractive as sorbents. The two important issues in sorbent applications are high adsorption capacity and efficient desorption. The main advantage of CNTs is that they are non-porous, and the solute is held on the surface by van der Wall's type forces. This eliminates the mass transfer resistance related to diffusion into the pore structures. The large specific capacity comes from the high aspect ratio of the CNTs. As a result, CNTs have been shown to be excellent high resolution gas chromatography stationary phases, which can separate a wide range of compounds from the very volatile to relatively large polycyclic aromatics (Haddon, 2002 and Miller, 2007).

The synthesis of CNTs generally involves the catalytic dissociation of organic precursors or graphite, during which other non tubular carbons (NTC), such as amorphous and graphitic carbon, are also formed. Often, the NTC is formed when the catalyst is exhausted, so most preparations include the CNTs coated with NTC on the surface. Unlike the CNT, the NTC tends to have porous structures, leading to different trapping mechanisms that can be diffusion controlled. So, purity of the CNTs is an important factor that influences the overall effectiveness as a sorbent (Saridara *et al.*, 2005 and Brukh *et al.*, 2006).

The breakthrough and desorption efficiency are important characteristics of a micro-sorbent trap (referred to as microtrap). Because of its small dimensions, only a small amount of sorbent can be packed inside, thus, making it prone to breakthrough. For quantitative sampling, the sample volume should not exceed its breakthrough volume (BTV), defined as the volume that can be sampled per unit weight of the sorbent before the analyte breaks through the sorbent bed. Previous studies have suggested that for a trap with a large number of theoretical plates, the breakthrough is independent of the analyte concentration. The microtraps are designed to be small, so that they have large number of plates and can be heated rapidly. Therefore, they are packed with a small amount of sorbent, often designed to retain the analytes only for a few seconds or minutes before rapid desorption. So, both adsorption and desorption play important roles in a fast-acting microtrap, and an understanding of these processes provides insight into the characteristics of these nano sorbents. The CNT sorbents can be used in a microtrap in a packed format, or as a self-assembled trap. The former facilitates the use of a larger amount of sorbent, while the latter provides an ordered nanostructure (Feng *et al.*, 1998; Ciucanu *et al.*, 2003; Kim *et al.*, 2003; Li *et al.*, 2003; Saridara *et al.*, 2005 and Karwa *et al.*, 2006).

The objective of this study was to develop CNT based microtraps for the online GC system and to study the sorption and desorption of selected volatile organic compounds on CNTs either packed or self-assembled within these micro-sorbent traps.

2. Experimental

2.1 Materials

A MWNT sample synthesized by CVD using ethanol as a precursor and Ni as catalyst was reported before (Hussain *et al.*, 2008). This sample, which was standardized, contained significant NTC and is referred to as MWNT-1. In an effort to eliminate the NTC and purify the CNTs, first the sample was passed through a 106 micron (Endecott, Ltd, England) sieve to eliminate the large particles. The NTC that remained on the CNT surface was removed by selective oxidation in a flow of air at 350°C for 30 min. The cleaned MWNT-1 is referred to as MWNT-1C. Purified SWNT and MWNT (referred to as MWNT-2) were purchased from Cheap Tubes Inc Carbopack^{TM}, which was purchased from Supelco Inc., was used as a basis for comparison.

2.2 Microtrap fabrication

The CNTs and Carbopack^{TM} were packed inside a 0.5 mm ID capillary to form a microtrap. Mechanical shaking using a vibrator was used to obtain a uniform packing. Each microtrap was packed with 20 mg of the sorbent. Self-assembled CNT microtrap was fabricated using a procedure reported before (Saridara *et al.*, 2005). Firstly, the steel tubing was heated in air at 10 mL/min flow at 500°C for 30 min to oxidize the surface. Then the surface was reduced in a 10 mL/min flow of H_2 at 500°C for 30 min. The oxidation and reduction led to the formation of a catalytically active surface. The chemical vapor deposition (CVD) was carried out at 700°C for

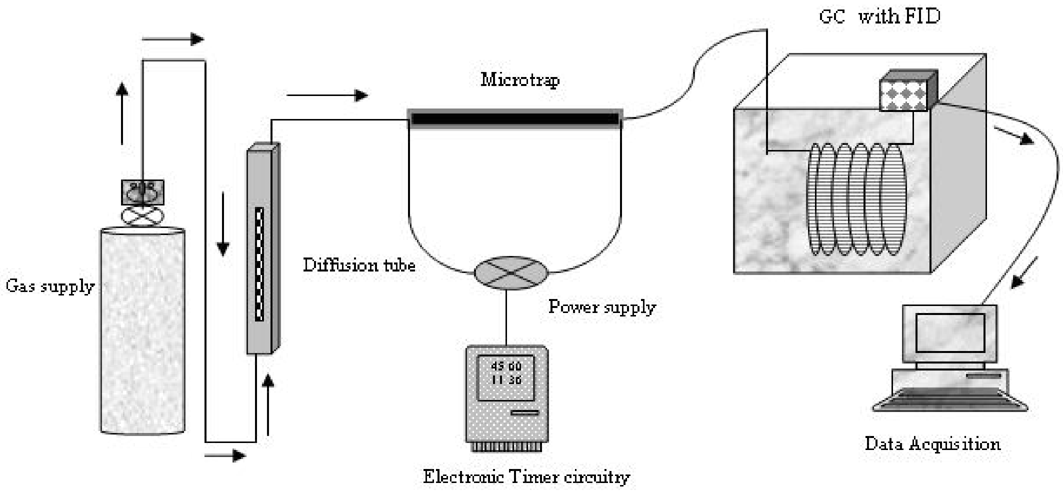


Figure 1. Schematic diagram of the experimental system.

1 hr. using C_2H_4 as the precursor. To remove the NTC from the CNT surface, a thermal annealing in the presence of oxygen was carried out at 350°C at a flow rate of 300 mL/min.

Scanning electron microscopy (SEM) using Model Genesis 4000 XMS (EFI, USA) was used to study the MWNT-1 and MWNT-1C. The SEM image of the self-assembled CNTs was obtained by a Leo 1530 VP (Carl Zeiss SMT AG Company, Oberkochen, Germany).

2.3 Experimental system

The experimental system is shown in Figure 1. Parts per million level organic compound standards were generated using a diffusion tube method reported in (Savitsky *et al.*, 1972). N_2 containing trace levels of VOCs were made by employing a diffusion dilution cell. Gas stream was passed over the mouth of the capillary at a known flow rate. As we know the capillary radius, the rate of diffusion of vapor into the gas stream at any given time can be calculated from the equation:

$$S = X \rho A/2L$$

where S = rate of diffusion (g/sec), X = slope (cm^2/min), ρ = density of sample (g/cm^3), A = cross section area of capillary (cm^2) and L = depth (cm). The value of X was experimentally determined for each VOC at different temperatures, and then the concentration was calculated as:

$$C = (SK)/F$$

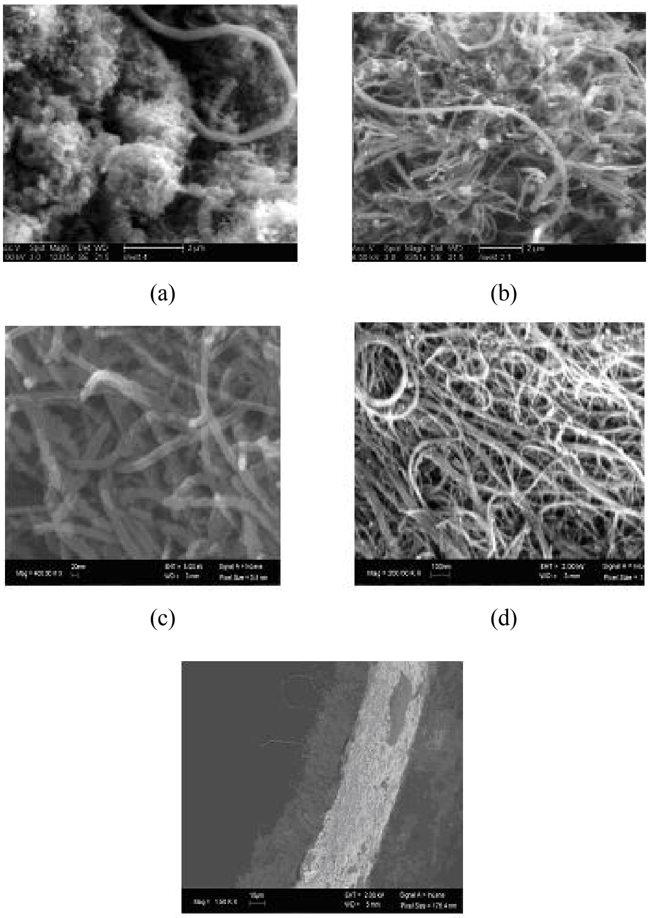
where C = concentration (ppm), K = 24.45/MW (molecular weight of VOC) and F = flow rate of gas (ml/min). The N_2 stream containing the organic compounds flowed through the microtrap continuously and the organic compounds were retained by the sorbents. Desorption pulses at fixed intervals were applied to the microtrap, so that the trapped organic compounds were desorbed and detected by the GC. The microtrap was resistively heated with a 7-10 ampere pulse of electric current from a power supply (Variac 100/200 Series). Typical duration of the electric pulse was between 1-1.5 seconds, and intervals varied between 2 and 20 min. An electric timer (Variac ATC 305) was used to control the frequency of injections. Different desorption temperatures could be achieved by increasing either the voltage or the duration of heating. Gas Chromatograph (Varian 3400) equipped with conventional flame ionization (FID) was used for analysis using a 0.53 mm. i.d., 30 m capillary column (DB-624, J&W Scientific). Nitrogen was used as the carrier gas at a flow rate of 3 mL/min.

3. Results and Discussion

3.1 Purifications of CNTs

Figure 2(a), shows the SEM image of MWNT-1, which appears to be covered with NTC. Some of it comprised large agglomerates of several microns in diameter. With few available CNT sites, much of the adsorption would be expected to occur on the NTC. Different purification strategies were employed to clean MWNT-1. Figure 2(b) is the SEM of MWNT-1C, which had been cleaned by sieving to remove the large particles, and then oxidized in air at 350°C to eliminate the amorphous carbon on the surface. This preparation showed mainly CNTs with some residual NTC. Too long exposure to air at high temperature led to the oxidation of the MWNT as well, so the heating time was limited to 30 min. With these two purification steps, the availability of the active CNT sites increased dramatically.

The SEM images of the MWNT-2 and SWNT are presented in Figures 2(c) and 2(d) respectively, which show relatively pure preparations that did not require any prepro-



(a) (b)

(c) (d)

(e)

Figure 2. SEM images of; (a) MWNT-1, (b) MWNT-1C, (c) MWNT-2, (d) SWNT and (e) self-assembled CNTs.

cessing. The length of the CNTs ranged from a few hundred nanometers to micrometers while the average diameter range of 10-20 nm for SWNT and 20-40 nm for MWNTs.

Figure 2(e) shows the SEM image of self-assembled CNTs inside the microtrap. This image was taken after the oxidative cleaning by passing air at 350°C. The CNTs were vertically aligned in a forest-like structure providing excellent sorption sites. The average diameter for self-assembled CNTs were much smaller than that of MWNT-1C. The film thickness of self-assembled CNTs was found to be about 20 microns, and they were uniformly distributed throughout the microtrap.

The characteristics of the different CNTs in terms of their surface area, average diameter and length are presented in Table 1. SWNT and MWNT-2 had the higher BET (Brunauer, Emmett and Teller) surface area as compare to other nanotubes (MWNT -1C) and Carbopack^{TM}.

3.2 Breakthrough characteristics of the microtrap

As the N_2 continuously flowed through the microtrap, the organic compounds already trapped in the microtrap began to migrate because the N_2 acted as an eluent. The sorption capacity of the CNTs in the microtrap was evaluated by studying the breakthrough time of the microtrap, which is defined as the time required by an analyte to elute through, or the time for which the organic compounds are retained on the CNTs (Xu *et al.*, 1994). To calculate the breakthrough time (t_b) of a microtrap several equations have been suggested. The basic principle of these is based on the mass balance between the flowing stream introduced at the head of the microtrap and the sum of the analytes retained by trap and the flowing stream pass through the microtrap. The breakthrough time is expressed as

$$t_b = \frac{W_c}{C_0 Q}\left[W_s - \frac{\rho Q}{K\gamma}\ln\left(\frac{C_0 - C}{C}\right)\right] \qquad (1)$$

where W_s is the weight of sorbent (mg), W_c is the sorption capacity (mgg^{-1}), Q is the flow rate of the carrier gas (mL/min), ρ is the density (gm/L), Kγ is the sorption rate constant /min), Co is the inlet concentration (mg/mL), and C is the breakthrough concentration mg/mL) (Ciucanu *et al.*, 2003). The breakthrough volume is also a product of breakthrough time and flow rate, so it is directly proportional to the latter. The breakthrough time is a function of the capacity factor, length and flow rate (Saridara *et al.*, 2005). It was measured by operating the microtrap at different injection intervals. Increasing injection interval enhanced the detector response as more organic compounds were accumulated by the microtrap. Once the VOCs began to breakthrough, the response did not increase any further with the interval. So the breakthrough time of the microtrap was computed as the time required to reach the maximum response (Guo *et al.*, 1998).

Table 1. Characteristics of the different carbon nanotubes used in the microtraps.

Type of Sorbent	Surface Area (m^2/g)	Average Diameter (nm)	AverageLength (μm)
MWNT -1C	110	150-175	morethan 10
MWNT-2	233	20-40	10-30
SWNT	407	10-20	5-30
Self-assembled CNTs	----	20-50	10-20
Carbopack	100	----	----

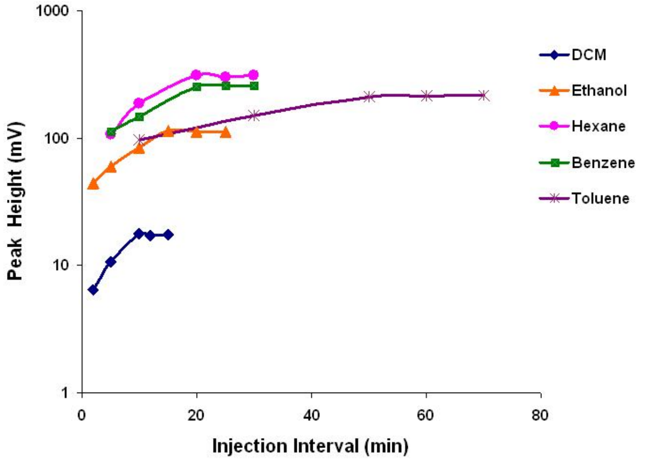


Figure 3. Detector response as a function of injection interval for the SWNT microtrap; the microtrap was filled with 20 mg of sorbent and heated for 1.5 seconds by applying a 10 ampere electric current at 25°C, while VOCs stream was flowing continuously through microtrap.

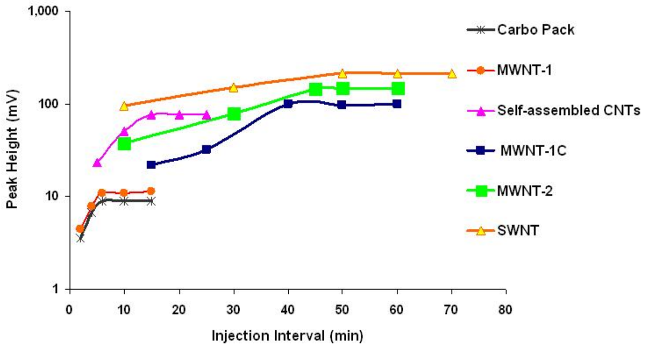


Figure 4. Detector response as a function of injection interval for toluene using microtraps containing different sorbents; the microtrap was filled with 20 mg of sorbent and heated for 1.5 seconds by applying a 10 ampere electric current at 25°C, while toluene was flowing continuously through microtrap.

Five organic compounds representing a wide range of volatility with varying polarity were analyzed. Typical breakthrough profiles for SWNT at 25°C are seen in Figure 3, with toluene showing the longest breakthrough time. Sorptions on other CNTs were similar, and are not presented here for brevity. The comparison of different sorbents with respect to the retention of toluene at 25°C is shown in Figure 4. For the same mass of sorbent, all the CNTs showed significantly higher sorption capacity compared to Carbopack, the only conventional sorbent in the group. The impure MWNT-1 with large amount of NTC was similar to the Carbopack as much of the adsorption occurred on the NTC, which was morphologically closer to Carbopack than the CNTs. The purification to MWNT-1C led to a 600% increase in breakthrough time. This shows the importance of impurity elimination when it comes to the use of CNTs. The self-assembled CNTs showed relatively high sorption capacity in spite of the fact that it was only a 20 µm thick film and represented a small quantity of CNTs. The breakthrough times for different compounds on the different sorbents at 25°C are listed in Table 2.

The SWNT showed the highest adsorption capacity, in terms of breakthrough volume. This is attributed to the higher aspect ratio due to the smaller diameter, which led to the higher specific area. For example, the breakthrough time of DCM on SWNT was five times higher than that on Carbopack or MWNT-1. MWNT-1C showed breakthrough times that were closer to MWNT-2, but were consistently lower. This was attributed to higher impurities in the MWNT-1C, along with other factors, such as different size and morphology. The retention of C_6H_6 was lower than expected, but that of xylene was quite high. The aromatic compounds were expected to have relatively stronger interactions with CNTs (Saridara *et al.*, 2005). Although benzene and hexane exhibited similar breakthrough times, xylene showed significantly longer breakthrough times. From Tables 1 and 2, it appears that the breakthrough times were not directly related to the BET surface area. For example, the specific surface area of SWNT was significantly higher than MWNT-2, but for many of the compounds studied here, the breakthrough times were quite similar.

3.3 Desorption from the microtrap

The desorption of organic compound is also an important factor. It was achieved by passing a pulse of electric current directly through the wall of the microtrap. For desorp-

Table 2. Breakthrough times (minutes) for different sorbents and analytes at 25°C.

Type of Microtrap	DCM	Ethanol	Hexane	Benzene	Toluene	Xylene
MWNT-1C	5	10	15	15	40	120
MWNT-2	8	12	20	20	45	120
SWNT	10	15	20	20	50	120
MWNT-1	2	2	5	6	6	10
Carbopack	2	2	5	6	6	10
Self-assembled CNTs	2	5	6	10	15	20

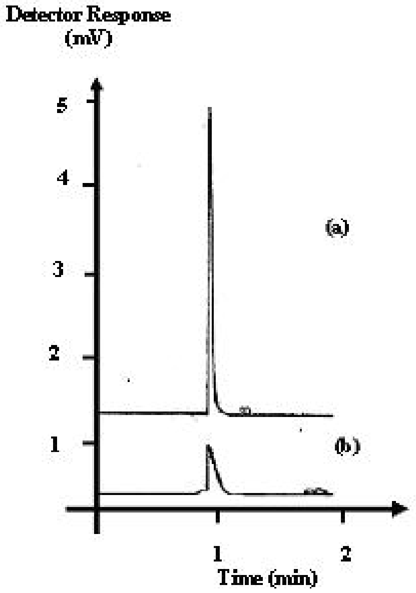


Figure 5. Desorption profile of toluene with different sorbents inside microtrap; (a) SWNT (b) Carbopack; the microtrap was filled with 20 mg of sorbent and heated for 1.5 seconds by applying a 10 ampere electric current at 25°C.

tion, enough energy needs to be provided (Ciucanu *et al.*, 2003). Figure 5 shows typical desorption profile of toluene generated from these sorbents. The peak width is a measure of the ease of desorption, and is also an important parameter in chromatographic separation.

The higher desorption suggests that the sorption on the CNTs was more physical in nature, whereas for Carbopack the analyte held more strongly, thus limiting the complete desorption. Table 3 provides an interesting insight into the desorption of toluene and benzene from all the sorbents. Due to the mass transfer issues related to porous structures, both MWNT-1 and Carbopack showed the widest desorption bands, implying slow release of solutes. The desorption peak widths were lowest for SWNT. For toluene, the difference was 29%; however for benzene, this difference increased to more than 3.5 times. The very low desorption band widths from SWNT, MWNT-2 and MWNT- 1C prove that the CNTs are relatively easy to desorb and should provide higher desorption efficiency. Overall, the CNTs not only have high adsorption capacity but also are desorbed easily.

4. Conclusions

The study has suggested that the CNTs can be integrated with on-line GC system to provide continuous monitoring of VOCs. The carbon nanotubes are excellent for both strong adsorption and relatively rapid desorption of organic compounds. The former is characterized by high breakthrough times (or volumes). Similarly, rapid desorption from CNTs was demonstrated by narrow desorption band widths. The elimination of NTC and disordered carbon from the CNT surface is quite important, as they reduce the performance of these sorbents. Both single and multi-walled tubes showed excellent performance during adsorption as well as desorption.

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References

Brukh, R., Salem, T., Slanvetpan, T., Barat, R. and Mitra, S. 2002. Process modeling and on-line monitoring of benzene and other species during the two-stage combustion of ethylene in air. Advances in Environmental Research. 6, 359-367.

Brukh, R. and Mitra, S. 2006. Mechanism of carbon nanotube growth by CVD. Chemical. Physical. Letters. 424, 126-132.

Ciucanu, I., Caprita, A., Chiriac, A. and Barna, R. 2003. Helical Sorbent Microtrap for Continuous Sampling by a

Table 3. Peak width at half height for toluene and benzene

Type of Microtrap	Toluene[1] (Seconds)	Benzene[2](Seconds)
Self-assembled CNTs	1.88	0.275
MWNT-1C	1.87	0.28
MWNT -2	1.7	0.265
SWNT	1.6	0.26
MWNT-1	2.05	1.87
Carbopack	2.06	1.89

1. Flow rate of 3 mL/minutes
2. Flow rate of 6 mL/minutes

Membrane and Trap Interface for On-Line Gas Chromatographic Monitoring of Volatile Organic Compounds. Analytical Chemistry. 75, 736 -741.

Chen, C. and Huang, C. 2007. Hydrogen storage by KOH-modified multi-walled carbon nanotubes. International Journal of Hydrogen Energy. 32, 237-246.

Düren, T., Sarkisov, L., Yaghi, O. M. and Snurr, R. Q. 2004. Design of New Materials for Methane Storage. Langmuir. 20, 2683 -2689.

Feng, C. and Mitra, S. 1998. Breakthrough and desorption characteristics of a microtrap. Journal of Chromatography A. 805, 169-176.

Guo, X. and Mitra, S. 1998. Development of pulse introduction membrane extraction for analysis of volatile organic compounds in individual aqueous samples, and for continuous on-line monitoring. Journal of Chromatography A .826, 39-47.

Guo, X. and Mitra, S. 1999. Theoretical Analysis of Non-Steady-State, Pulse Introduction Membrane Extraction with a Sorbent Trap Interface for Gas Chromatographic Detection. Analytical Chemistry. 71, 4587-4593.

Haddon, R.C. Carbon nanotubes. 2002. Accounts of Chemical Research. 35, 977-1113.

Hussain, C. M., Saridara, C. and Mitra, S. 2008. Microtrapping Characteristics of Single and Multi-Walled Carbon Nanotubes. Journal of Chromatography A .1185, 161-166.

Kim, M. and Mitra, S. 2003. A microfabricated microconcentrator for sensors and gas chromatography. Journal of Chromatography A. 996, 1-11.

Karwa, M. and Mitra, S. 2006. Gas Chromatography on Self-Assembled, Single-Walled Carbon Nanotubes, Analytical Chemistry. 78, 2064-2070.

Li, Q. and Yuan, D. 2003. Evaluation of multi-walled carbon nanotubes as gas chromatographic column packing. Journal of Chromatography A. 100, 203-209.

Mitra, S. and Yun, C. 1993. Continuous gas chromatographic monitoring of low concentration sample streams using an on-line microtrap, Journal of Chromatography. 648, 415-421.

Miller, G. P. Carbon Nanotubes, Properties and Applications. 2007. Journal of American. Chemical. Society. 129, 6343-6344.

Savitsky, A. C. and Siggia, S. 1972. Improved diffusion dilution cell for introducing known small quantities of liquids into gases. Analytical Chemistry. 44, 1712-1713.

Subramoney, S. 1998. Novel nano-carbons-structure, properties, and potential applications. Advance Materials.15, 1157-1171.

Saridara, C., Brukh, R., Iqbal, Z. and Mitra, S. 2005. Preconcentration of Volatile Organics on Self-Assembled, Carbon Nanotubes in a Microtrap. Analytical Chemistry. 77, 1183-1187.

Thammakhet, C., Thavarungkul, P., Brukh, R., Mitra, S. and Kanatharana, P. 2005. Microtrap modulated flame ionization detector for on-line monitoring of methane. Journal of Chromatography A. 1072, 243-248.

Xu, Y. H. and Mitra, S. 1994. Continuous monitoring of volatile organic compounds in water using on-line membrane extraction and microtrap gas chromatography system. Journal of Chromatography A. 688, 171-180.