การนำท่อนาโนคาร์บอนซึ่งมีพฤติกรรมการดูดซับสูงไปเป็นตัวดูดซับสำหรับประยุกต์ใช้ทางด้านสิ่งแวดล้อม

นาย ชอดรี มุซตันซาร์ ฮุแซน

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
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CARBON NANOTUBES AS HIGH PERFORMANCE SORBENTS FOR ENVIRONMENTAL APPLICATIONS

Mr. Chaudhery Mustansar Hussain

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By	Mr. Chaudhery Mustansar Hussain
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Advisor	Professor Somenath Mitra, Ph.D.
Co-advisor	Assistant Professor Chutarat Saridara, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

……………………………………Dean of the Graduate School
(Associate Professor Pornpote Piumsomboon, Ph.D.)

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Chutarat Saridara
…………………………………………………Co-advisor
(Assistant Professor Chutarat Saridara, Ph.D.)

……………………………………………….. Examiner
(Chantra Tongcumpou, Ph.D.)

B. Kitiyanan
……………………………………………….. Examiner
(Assistant Professor Boonyarach Kitiyanan, Ph.D.)

Nuttapun Supaka
…………………………………………………External Examiner
(Nuttapun Supaka, Ph.D.)

ชอตรี มุชตันซาร์ ฮุแซน : การนำท่อนาโนคาร์บอนซึ่งมีพฤติกรรมการดูดซับสูงไปเป็นตัวดูดซับสำหรับประยุกต์ใช้ทางด้านสิ่งแวดล้อม (CARBON NANOTUBES AS HIGH PERFORMANCE SORBENTS FOR ENVIRONMENTAL APPLICATIONS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: Prof. Somenath Mitra, Ph.D, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ.ดร.จุฑารัตน์ ศริดารา, 105 หน้า.

ในด้านสิ่งแวดล้อมแล้วกลุ่มสารอินทรีย์ระเหยง่าย(VOCs)และกลุ่มสารอินทรีย์ระเหยยาก(SVOCs)นั้นมีความสำคัญมากทั้งนี้เนื่องจากมันสามารถแพร่กระจายจากแหล่งกำเนิดผ่านทางตัวกลางต่างๆ ได้หลายชนิด และถึงแม้จะมีความเข้มข้นเพียงเล็กน้อยมันสามารถทำอันตรายแก่มนุษย์และระบบนิเวศน์ได้ การที่จะตรวจวัดสารความเข้มข้นน้อยๆเหล่านี้ได้เป็นงานที่มีความท้าทายมากและจำเป็นต้องใช้เครื่องมือการตรวจวัดชนิดออนไลน์ที่มีความเร็วสูง ในการศึกษานี้เป็นการประเมินผลกระทบทางด้านสิ่งแวดล้อมโดยการประยุกต์ใช้ท่อนาโนคาร์บอน(CNT)บรรจุภายในไมโครแทรปเชื่อมต่อเป็นระบบออนไลน์แก๊ซโครมาโตกราฟีใช้สำหรับตรวจวัดตัวอย่างสารที่ดูดซับไว้ได้จากสิ่งแวดล้อมอันได้แก่กลุ่มสารอินทรีย์ระเหยง่ายและสารอินทรีย์ระเหยยาก การประยุกต์ดังกล่าวนี้พัฒนาขึ้นสำหรับใช้ในการตรวจวัดกลุ่มสารดังกล่าวเพื่อลดการปนเปื้อนและความคลาดเคลื่อนที่เกิดขึ้นในขั้นตอนการเก็บตัวอย่าง การขนย้าย การเก็บรักษาตัวอย่าง และการทดลองในห้องทดลอง รวมทั้งเป็นการจัดเตรียมระบบการวิเคราะห์ที่เป็นอัตโนมัติและสามารถวัดสารปริมาณน้อยๆได้สำหรับการวิเคราะห์สารอินทรีย์ระเหยง่ายและกลุ่มสารอินทรีย์ระเหยยาก

ท่อนาโนคาร์บอนเป็นตัวดูดซับที่ถูกนำไปใช้ในด้านต่างๆอย่างแพร่หลาย และส่วนใหญ่ถูกประยุกต์ใช้ในขั้นตอนการเตรียมสารปริมาณน้อยๆให้มีความเข้มข้นเพียงพอสำหรับการวิเคราะห์ คุณสมบัติที่เด่นชัดอย่างหนึ่งของท่อนาโนคาร์บอนคือความไม่มีรูพรุนทำให้ลดกระบวนการเคลื่อนย้ายมวล อันเป็นผลมาจากกรณีของการที่โมเลกุลของสารแพร่เข้าไปในโครงสร้างที่เป็นรูพรุนและนั่นเองที่ทำให้ท่อนาโนคาร์บอนเป็นตัวดูดซับที่มีประสิทธิภาพสูง ไมโครแทรปนั้นเป็นท่อโลหะขนาดเล็กมากซึ่งบรรจุเอาตัวดูดซับปริมาณเพียงเล็กน้อยเอาไว้ภายใน มันถูกออกแบบมาเพื่อการเตรียมสารที่มีความเข้มข้นน้อยๆให้มีความเข้มข้นมากขึ้นพอที่จะวิเคราะห์ได้ โดยถ้าเป็นระบบออนไลน์มันจะถูกฉีดเข้าไปเครื่องแก๊ซโครมาโตกราฟีเพื่อการวิเคราะห์ต่อไป การบรรจุท่อนาโนคาร์บอนเข้าไปในไมโครแทรปนั้นมีหลายวิธี ทั้งการบรรจุเข้าไปโดยตรง(packed)หรือบรรจุผงคาร์บอนที่ยังไม่เป็นท่อนาโนคาร์บอนลงไปก่อนแล้วจึงทำให้เป็นท่อนาโนคาร์บอนขณะที่อยู่ภายในไมโครแทรปหรือเรียกกระบวนการนี้ว่า self assembled แล้วจึงทำการศึกษาเปรียบเทียบคุณสมบัติของท่อนาโนคาร์บอน แบบบรรจุโดยตรง และ self assembled

จากการทดลองตรวจวัด สารกลุ่มสารอินทรีย์ระเหยง่าย ด้วยเครื่องแก๊ซโครมาโตกราฟี โดยใช้ ไมโครแทรป ที่บรรจุด้วยท่อนาโนคาร์บอนจากทั้งสองแบบเป็นตัวดูดซับ พบว่าท่อนาโนคาร์บอนนั้นมีประสิทธิภาพสูงในการดูดซับและปลดปล่อยที่เร็วมาก ทั้งยังมีผลการทำซ้ำที่ดีและมีความเสถียรสูง แต่การเกิดท่อปิดนั้นถ้าไม่กำจัดออกจากผิวหน้าแล้วจะทำให้ประสิทธิภาพในการดูดซับลดลง ในงานวิจัยนี้ยังแสดงให้เห็นว่าท่อนาโนคาร์บอนทั้งชนิดซิงเกิลวอลล์และชนิดมัลติวอลล์ที่ใช้บรรจุในไมโครแทรปทั้งแบบบรรจุโดยตรงและ แบบ self-assembly นั้นทั้งสองชนิดสามารถพัฒนาเพื่อใช้ในงานวิเคราะห์ทางสิ่งแวดล้อมและการวิเคราะห์ด้านอื่นๆได้เป็นอย่างดี ดังนั้นการศึกษานี้ จึงเป็นการเริ่มต้นพัฒนาสู่การวิเคราะห์ในระบบการดูดซับประสิทธิภาพสูงโดยมีการใช้ท่อนาโนคาร์บอนเป็นทางเลือกใหม่ของตัวดูดซับในงานวิเคราะห์และตรวจวัดด้านสิ่งแวดล้อม

นอกจากนี้ยังมีการศึกษาในเชิงลึกโดยการเปลี่ยนแปลงพื้นผิวของไมโครแทรปซึ่งสามารถทำได้โดยใช้ขบวนการ microwave acid chemistry ร่วมกับหมู่ฟังก์ชั่นในท่อนาโนคาร์บอน มีผลทำให้ธรรมชาติของพื้นผิวท่อนาโนคาร์บอนมีการเปลี่ยนแปลงไปทำให้มีปฏิกิริยาร่วมกันมากขึ้นซึ่งก่อให้เกิดการคัดเลือกสรรสารอินทรีย์ได้เฉพาะเจาะจงมากขึ้นซึ่งจะเห็นได้อย่างชัดเจนในสารที่มีขั้วว่าทั้งประสิทธิภาพการดูดซับและการปลดปล่อยดีขึ้นอย่างชัดเจน

ในการศึกษาครั้งนี้พบว่ากระบวนการทำให้บริสุทธิ์และการเพิ่มหมู่ฟังก์ชั่นนั้นจะเป็นการเพิ่มเซนท์ซิติวิตี้ให้กับท่อนาโนคาร์บอนและทั้งการดูดซับทางกายภาพและการดูดซับทางเคมีของโมเลกุลของสารอินทรีย์นั้นมีความเป็นไปได้ทั้งคู่ แต่อย่างไรก็ตามการดูดซับทางกายภาพนั้นดูเหมือนจะมีบทบาทสำคัญมากกว่าทั้งนี้เป็นเพราะประสิทธิภาพของการปลดปล่อยที่ดีเยี่ยมของท่อนาโนคาร์บอน การค้นพบที่สำคัญของงานวิจัยนี้คือการแสดงให้เห็นว่าสามารถที่จะนำท่อนาโนคาร์บอนไปประยุกต์ใช้ในงานด้านสิ่งแวดล้อมได้จริงโดยใช้ร่วมกับระบบออนไลน์แก๊ซโครมาโตกราฟี

ภาควิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต ....

ปีการศึกษา 2551 ลายมือชื่อที่ปรึกษาวิทยานิพนธ์หลัก....................................

ลายมือชื่อที่ปรึกษาวิทยานิพนธ์ร่วม....................................

4789482320 : MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS: CARBON NANOTUBES/ SORBENT/ MICROTRAP/ GAS CHROMATOGRAPHY/ ONLINE MONITORING SYSTEM / ADSORPTION./ DESORPTION

CHAUDHERY HUSSAIN: CARBON NANOTUBES AS HIGH PERFORMANCE SORBENTS FOR ENVIRONMENTAL APPLICATIONS. ADVISOR: PROF. SOMENATH MITRA, Ph.D., COADVISOR: ASST. PROF.CHUTARAT SARIDARA, Ph.D., 105 pp.

From an environmental perspective the volatile organic compounds (VOCs) and semi volatile organic compounds (SVOCs) are very important. They can disperse from their sources in any media, and even at trace concentrations they are a threat to the humans and the ecosystem. The measurement of these organics at trace level is a major challenge and there is a need for instruments for rapid, on-line monitoring of these pollutants. This study evaluated the environmental applications of carbon nanotubes (CNTs) through the integration these inside microtrap for on-line gas chromatography system for monitoring of representative environmentally relevant adsorbates, volatile and semi volatile organic compound. The motivation behind such development is to eliminate contamination and errors associated with sample collection, transport, storage, and laboratory and to provide an automatic and sensitive system for monitoring of VOCs and SVOCs.

Carbon nanotubes (CNTs) possess several highly desirable sorbent characteristics, which makes them attractive for a variety of applications including as micro-scale preconcentration. The main advantage of CNTs is that they are non-porous, thus eliminating the mass transfer resistance related to diffusion into pore structures. Their high aspects ratio leads to large specific capacity, consequently they have the potential to be the next high performance sorbent. A microtrap is small metal capillary tubing containing a small amount of sorbent. The microtrap is 'designed for preconcentration the analyte from flowing containing stream as well as moduled for an injector for gas chromatography (GC), when uses for on-line system. Variety of CNTs inside microtraps either packed or self assembled format for the online detection of gas chromatography system were developed. A comparative study between packed CNTs and self-assembled CNTs has performed.

The results obtained from developed microtraps with variety of CNTs sorbents for on-line GC system of organics, have shown high-capacity adsorption and fast quantitative desorption, and the process exhibited good reproducibility and long time stability. The elimination of non tubular carbons (NTC) from the CNT surface is important, as they reduce the performance of these sorbents. This research has explained that CNTs either single (SWNT) or multi-walled (MWNT) with both formats (packed or self-assembled) can be used for analytical applications in environment, and these can work as efficiently as other analytical techniques. Consequently, this will open the doors to the application of high-capacity, CNTs-based sorbents as an alternative to other sorbent in environmental monitoring and analysis.

To evaluate further in-depth knowledge of the microtrapping phenomenon, apart from pure CNTs, the strategy of surface modification was employed and that was achieved through the process of microwave acid chemistry . Incorporation of functional groups on CNT has altered their surface nature which allows greater number of interactions and consequently changes their selectivity towards organic molecules and both sorption and separation efficiency for polar analytes was increased dramatically.

This work suggests the process of purification and functionalization can influence the sensitivity of CNTs towards their microtrapping characteristics. Both physisorption and chemisorption of organics on nanotubes were possible, however, physisorption was seem to be more dominant as reflects from the excellent desorption efficiency of CNTs. The key findings of this work show the realistic environmental applications of CNTs by integrating them with online GC system.

Field of study : Environmental Management Student's signature...

Academic year :..........2008.............. Advisor's signature...

Co-advisor's signature.........Chutarat Saridara.........

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NOMENCLATURE

Symbol / abbreviation	**Name**
VOCs	Volatile Organic Compounds
SVOCs	Semi Volatile Organic Compounds
USEPA	United States Environmental Protection Agency
CAAA	Clean Air Act Amendments
GC-FID	Gas Chromatography Flame Iodization Detector
GC/MS	Gas Chromatography Mass Spectroscopy
CVD	Chemical Vapor Deposition
CNTs	Carbon Nanotubes
SWNT	Single Walled Carbon Nanotubes
MWNT	Multiwalled Carbon Nanotubes
f-MWNT	Functionalized Multiwalled Carbon Nanotubes
NTC	Non Tubular Carbon
ID	Internal Diameter
BTV	Breakthrough Volume
PPM	Parts Per Million
sec	Second
min	Minute
mL	Milliliter
TEM	Transmission Electron Microscopy
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis
FTIR	Fourier Transformation Infrared
kJ/mole	Kilo Joule Per Mole
H_2	Hydrogen
$C_2\ H_4$	Ethylene
DCM	Dichloromethane
mL/min	Milliliter Per Minute
N_2	Nitrogen
O_2	Oxygen
m	Meter
µm	Micro Meter
nm	Nano Meter
^oC	Centigrade
BET	Bet (Brunauer, Emmett, And Teller) Surface Area
T	Absolute Temperature
ΔH_s	Isosteric Heat Of Adsorption
R	Gas Constant
$W\ m^{-1}\ K^{-1}$	Watt Per Meter Per Kelvin
V	Volts
m^2/g	Meter Square Per Gram
EDTA	Ethylene Diamine Tetra-Acetate (EDTA)
psi	Pressure Per Square Inch
DMF	Dimethylformamide

THF	Tetrahydrofuran
t_b	Breakthrough Time
mgg^{-1}	Milligram Per Gram
gmL^{-1}	Gram Per Liter
$mgmL^{-1}$	Milligram Per Milliliter
RSD	Relative Standard Deviation

CHAPTER I

INTRODUCTION

1.1 Statement of Problem

Volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) include a variety of organic molecules with different functional groups. Many of them are classified as hazardous air pollutants (HAPs) by the United States Environmental Protection Agency (US EPA), and regulated by the Clean Air Act Amendments (CAAA) of 1990. They can cause eye, nose, and throat irritation, headaches, nausea, and damage to liver, kidney, and central nervous system. Some organics, such as benzene, methylene chloride and perchloroethylene, are known to cause cancer in animals and in humans [1]. Furthermore, organics cause serious health problems by photochemical reactions that form ground-level ozone, which is the principal component of smog. Ozone pollution (smog) causes severe health and environmental problems, such as respiratory problems, damaging crops and plants, ruining the city landscape. In addition, some organics play an important role in global warming and in destruction of the stratospheric good ozone [2].

Organics are encountered virtually everywhere. The consumer items, the energy-sources, and the drink water (because of the reaction between chlorine used for water disinfection and organic matter in water) all increase human exposure to these compounds. The combination of ubiquitous exposure and possible serious health effects has long been making organics a major public health issue [3].

In 1997, the US government approved strong new clean air standards for smog and soot, which could prevent up to 15,000 premature deaths a year and improve the lives of millions of Americans who suffer from respiratory illnesses. To achieve this goal, the US EPA implemented emission factors and emission inventories as fundamental tools/concepts in air quality management. These tools are important for developing emission control strategies, determining the applicability of permitting and control programs, and ascertaining the effects of sources and appropriate mitigation strategies. Policies on reduction of pollution can only be designed when the extent and identity of the pollutants is known. Emissions can only be regulated based on accurate and reliable methods for monitoring the emitted materials. Therefore, measurement and analysis of organics is the cornerstone for protecting public health and the environment [4].

The development of rapid and sensitive analytical instrumentation is necessary to monitor the ambient organics in the environment and to monitor emission sources. Traditional methods to analyze for organics in ambient air and stack emissions use either whole air samplers such as 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 associated with sampling, sample transport and storage. Furthermore, most of these techniques require extensive sample handling, which increases the analysis cost per sample. For process environmental monitoring and process control, the analytical results are critical and the information is needed as soon as possible. On-line monitors can almost immediately detect an upset in a chemical process, so that corrective actions may be taken. Not only does this reduce environmental problems, but it can also save industry money in terms of resource conservation and recovery [5]. 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.

1.2 Research objectives

The objective of this study was to develop Carbon nanotubes (CNTs) based microtraps for the on-line GC system with an aim to investigate the environmental applications of CNTs as micro-sorbent. A better understanding of the breakthrough and desorption characteristics is required for CNT microtraps. A goal is to develop an understanding of breakthrough as a function of sorption capacity of CNTs within microtrap while desorption mechanisms were established through desorption profiles. The key findings of these studies will then be extended to more possible applications via complex systems. A long term goal of the study is to design more efficient and cost-effective micro-sorbents, e.g. carbon nanotubes, for pollution prevention and control schemes through the basic understanding of these materials.

In summary the objectives of this research was of three folds:

- To develop the carbon nanotubes (CNTs) based microtraps.
- To study the microtrapping characteristics of CNTs using different organic compounds for online gas chromatography system.
- To compare the different configuration of CNTs, synthesized either in laboratory or commercially available, to have in-depth knowledge of trapping phenomenon of organic molecules on CNT surface.

1.3 Hypothesis

Carbon nanotubes (CNTs) have exceptional small sizes, large surface areas, hollow and nano-sized layered structures, high mechanical strength and excellent adsorptive ability which make them a promising material for variety of applications, especially, as sorbents in environmental analysis. Thus, it is believed that CNTs can be better alternative to conventional sorbents inside the microtrap for online GC system.

1.4 Scope of the study

The scope of this research is to develop high performance sorbents like CNTs which will be helpful in real time monitoring of VOC and SVOC at trace levels in any media. The motivation behind such development is to eliminate contamination and other errors during sampling and transportation. The scope of this study is three fold as follows:

1. Fabrication of CNT based microtrap where CNT were synthesized by CVD system either in laboratory or commercially available.
2. Evaluation the performance of CNTs as micro-sorbent by studying their microtrapping characteristics by using VOCs and SVOCs.
3. Evaluation of different configurations of CNTs to have in depth knowledge of micro-sorption of organic molecules on CNTs.

CHAPTER II

LITERATURE REVIEW

2.1 On-line Monitoring System and its importance

Evolving environmental regulations and the rising costs of compliance testing are pushing environmental scientist to explore the application of new, more cost-effective technology. Recently there has been much effort in the development of analytical techniques for continuous, on-line measurement of organics in air emission and in ambient air. The first consideration for these developments is the speed of analysis. Typically laboratory analysis has a turn around time of several days and the data can not be used for taking corrective actions in a process. The turn around time is of the order of a few minutes or even a few seconds for most on-line methods. In other words, on-line monitoring is valuable in monitoring emission transients and also in implementing process control [6-7].

Another consideration is cost. The strict reliance on off-site laboratory analysis of collected samples contributes to this lengthy process. Typically, samples are collected in the field and sent to a laboratory for analysis. On an average 70 % of the samples collected are nondetects, containing no contaminants. Therefore, additional trips must be made to collect samples for analysis in order to obtain an adequate information about the site. Considering all these factors, with prudent use of field analysis, the cost of environmental testing can be reduced significantly [8].

The other consideration for using on-line monitoring technique is accuracy. Analyte concentrations can degrade during the period between sample collection and its chemical analysis. These concentration changes are complex and are related to such factors as analyte volatilization, analyte kinetics, biodegradation, container leakage, preservation conditions, extraction efficiency, and analytical accuracy. During transport and storage of sample, the sample can degrade and contamination can occur. For example, many organic compounds, especially the polar compounds, are known to be unstable in canisters [9].

From this standpoint, even if the precision of an on-line method is not as good as that of a lab method, it still provides more accurate results than a conventional lab method because transportation and storage are eliminated.

Table 2.1 Description of advantages and disadvantages of off-line and on-line preconcentration system

OFF-LINE Sample preconcentration steps are performed manually and sequentially and separated from each other and from the separation-plus-detection part of the system.	
Advantages - Samples can be worked up in parallel - Better optimization of individual steps - Simplicity of equipment - Operational flexibility	**Disadvantages** - No possibility of automation - Labour-intensive - Time-consuming - Aliquot of sample is analysed - Risk of solute losses - Risk of contamination
ON-LINE Sample preconcentration steps are directly connected with the separation-plus-detection part in a closed system, i.e. via connective microtrap tubing and valves etc.	
Advantages - Automation is possible - Risk of analyte losses is reduced - Contamination from external sources is minimized - Total sample is analysed, i.e. Analyte detectability is enhanced - Precision is improved	**Disadvantages** - Sequential process - Procedure has less flexibility - Optimization of individual steps is difficult

A significant trend in analytical chemistry today is away from the use of laboratory-based methods and instrumentation towards on-line, in-situ methods. The latter provide faster information, are less expensive and often more reliable than conventional techniques. A top priority in the environmental field is real-time analysis. This can be achieved by moving a laboratory to the field, or by using field-portable instrumentation to perform the measurement directly on site. Moving a laboratory is not an easy option. So the latter option is more desirable, especially since more and more technologies are available for on-site analysis. Table 2.1 briefly describes the advantages and disadvantages of off-line and on-line preconcentration system.

GC is generally considered to be slow for continuous, on-line monitoring [10]. However, in the cases when continuous data is required to be reported on an hourly or every few minutes, GC is sufficiently fast. The further development of GC in real or near real-time monitoring includes application of on-line sampling, injection technologies, and faster column separation.

To combine preconcentration and injection, a sorbent trap is placed in an on-line position with the subsequent GC analysis. One such technique is the combination of microtrap systems with GC. The microtrap is a small dimension tubing packed with one or more adsorbents. Due to its low thermal mass, it can be heated rapidly and allows immediate on-line injection of the trapped organics into a GC. These microtrap systems function not only as on-line injectors, but also as separator and concentrator. Membrane has been combined with a microtrap system to enable continuous GC monitoring of air and water. Measurements in these studies were taken every 5-10 minutes, necessitated by sampling and separation times. In a field air analysis, SPME has been combined with fast portable GC to reduce the sampling and analysis time to less than 15 minutes [11-13].

With recent developments, GC analysis has become more and more rapid (high speed), selective (high resolution), automated and field-portable. Therefore, GC is being employed nowadays in continuous on-site monitoring systems. This is achieved by using different techniques. Dual sampling loop or trap, coupled with dual

GC columns, realizes near-real-time analysis. Sensitivity, sample throughput and identification of overlapping peaks can be dramatically enhanced by simultaneous use of different types of column stationary phases and different types of detectors [14].

The near real-time analytical information can be used to facilitate chemical hazard assessments and to take mitigative actions during: (a) emergency responses to chemical spills; (b) remedial investigations and feasibility studies of hazardous waste sites; (c) removal operations at hazardous waste sites; (d) special investigative operations such as drum and tank head-space analysis; (e) soil gas analysis and fence line monitoring: (f) point source emission monitoring; and (g) fugitive emission monitoring. Therefore, fieldable instruments, procedures, and sampling methods should have the analytical, operational and value-added characteristics [15].

2.1.1 Instrumentation for on-line monitoring

On-line monitoring systems integrate three main subsystems: a sampling interface, an analyzer and a control and data analysis system. One method of classifying the system is by the type of sampling system. In general, the systems can be classified into extractive, in situ, and remote. In an extractive system, the sample is physically transported from the source, conditioned and then introduced into the analyzer. In order for an instrument to measure gas concentrations, the gas sample must be free of particulate matter. Moisture usually must be removed. This requires the use of valves, pumps, and other components necessary for gas transport and conditioning. In the case of in-situ systems, the interface is simpler, composed of flanges designed to align or support the monitor and blower systems used to minimize interference from particulate matter [16].

The continuous monitor can also be categorized by the frequency of the sampling interface. For process monitoring applications, continuous, on-line monitoring is required to capture data regarding transient process events. Continuous, on-line monitors differ in the kind of information that they report. Some of them are non-selective and respond to gross process characteristics such as total non-methane organic carbon (NMOC) or total chlorine content. Others fall into the category of speciation monitors that provide individual concentrations of process components. The need for speciation is often determined by environmental regulations where the relative toxicity or the potential of a particular compound for production of smog may dictate an individual quantitative measurement [17].

On-line monitors also need to have good engineering design to assure simple operation and maintenance. A number of analytical techniques are available that can be applied to continuous, on-line monitoring but they must also be amenable to automated operation and data analysis. Other important distinctions are the same as with any analytical instrument such as selectivity, detection limits, size and cost. The most common techniques used for continuous, on-line measurement of organics include direct FID-gas chromatography [18-20].

2.1.1.1 Gas Chromatography

Gas chromatography (GC) offers a large selection of excellent columns and detectors for a variety of different types of separations. GC has been used for process stream analysis since the 1950s. Unlike spectroscopic techniques in which a sample stream can continuously pass through the detection cell, a sample injection in the form of a pulse is needed for GC separation. The most common sample introduction device in continuous gas chromatography is gas sampling valve. Valves can automatically make injections from a sample stream intermittently into a GC column [21].However, sample valves have certain limitations. Being mechanical devices, they tend to wear during extended periods of operation. Another problem with sample valves is that they withdraw a small fraction of sample stream for injection into the GC. The sample size that is injected into the GC is between a few microliters to a couple of milliliters. Injection of a larger sample quantity causes excessive band broadening and degrades chromatographic resolution. A small injection volume results in small sample quantity and poor sensitivity. In many applications, especially in environmental monitoring, low concentrations are encountered and sample valves are found to be inadequate [22].

The other approach for continuous, on-line GC analysis employs a thermal desorption modulator placed before the analytical column. Modulators are in principle quite similar to cryogenic traps used in chromatography. The conventional purge-and-trap devices are designed to preconcentrate analytes from a sample or to sharpen an injection, whereas modulators are used to continuously modulate the concentration of analytes in a flowing stream. Chromatography using modulators does not need any injection device because the equivalent of an injection is generated internally within the flow stream. Potential advantages of using modulators are faster operation, smaller bandwidth, lower detection limit, and improved reliability [23]. Moreover, it is a continuous analysis technique as compared to conventional valves that offer intermittent analysis. Some of the problems associated with using low-capacity modulators are low modulation efficiency, low sensitivity, inability to modulate volatile components, and derivative peak shape. The increase in capacity factor of the modulator results in a change in the chromatographic peak shape and the modulation efficiency increases.

2.1.1.2 Microtrap

Recently sorbent traps have been widely used as injection devices for continuous, on-line gas chromatography [24]. A trap made by packing narrow metal tubing with adsorbents is placed in front of the GC column. When sample stream passes through the trap, organic compounds of interest can be adsorbed by the adsorbent. At the end of sampling, the trap is thermally desorbed to produce a concentration pulse as injection to GC column. The sorbent trap is not only an injection device that can make the analysis continuous, on-line, but also a preconcentrator that enriches the sample during sampling. Membrane combined with microtrap has also been developed for continuous, on-line Organics monitoring in air or water [25-26]. Simultaneous extraction and stripping of organics by membrane combined with microtrap injection have shown some advantages such as elimination of moisture in humid samples.

2.1.1.3 Sorbents for monitoring of organics

A wide range of solid sorbents have been used in the measurement of organics in air. Nevertheless, research on the development of new types of sorbents has been reported [27-28]. Just as promoting the establishment of Method TO-17, the developments in new adsorbents have greatly enlarged the application of sorbent-based sampling in air analysis. An ideal sorbent needs to have four main properties, i.e. infinite breakthrough volume (BTV) for the compounds to be sampled, complete desorption of the target compounds at moderate temperatures, no generation of artifacts and no retention of water vapor. Moreover, it must be possible to seal the sorbent completely from the atmosphere so that contamination before and after sampling can be excluded. No single available sorbent material meets all of these criteria. There is a tendency to use multiple sorbents, which allows one to focus on a wide range of organics.

In addition, financial considerations are taken into account during the development of adsorbents. This can be achieved by deriving adsorbents from inexpensive raw materials and chemical treatment. These raw materials include saccharose and cellulose [29], activated coals [30], and even natural crab shell [31]. The last one was evaluated as an adsorbent for preconcentrating airborne organics collected in a canister. The by-product of fullerenes production, fullerenes-extracted soot, was also applied as adsorbent to collecting organics in air [32]. This by-product results from fullerenes extraction from soot generated by graphitized carbon evaporating under arc discharge. Unlike graphite with regular lattice and graphitized carbon produced from carbon blacks, the fullerenes-extracted soot is complex multi-component mixture, which is abundantly porous and has a large specific area.

2.2 Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are rolled up tubular structures of carbon, the carbon atoms are placed in a graphene sheet that is made up of benzene-type hexagonal rings. A single walled carbon nanotube (SWNT) is a single sheet of graphene rolled up into a cylindrical tube while multi walled carbon nanotube (MWNT) consists of these multiple sheets rolled up inside each other. The distance between the sheets in the multi walled carbon nanotube is approximately the same as the distance between two layers of graphene in graphite. CNTs has some unique electrical properties since they can be either metallic or semi-conducting, depending on their chirality. The electrons in the metallic nanotubes are not scattered which gives ballistic transport, thus the conductance of a perfect CNT is not dependent of the length. They also have some impressive mechanical properties as the Young's modulus is estimated to be around 120 GPa [33-35]. Nanotubes are also very good conductors of heat, better than copper or even graphite. The exceptional combination of physical properties comes from the unique structure of nanotubes. Nanotubes are one of the strongest substances known. The properties described above are however only valid for perfect carbon nanotubes without defects. Real CNTs have a lot of defects in them. The defects are typically dislocations where the crystal structure is disordered or vacancies where carbon atoms are missing in the crystal structure or impurities where other atoms either replace or sit in between the carbon in the lattice. These different defects will cause the electrons to be scattered so the electrical transport is rarely ballistic. Also the mechanical properties are weakened. [36-37].

2.2.1 Carbon nanotubes (CNTs) Growth

CNTs are mostly grown by three different methods. All three of them has the same basic concept which is to get free carbon from a carbon material e g , solid or gas, to realign as carbon nanotubes, since CNTs are energetically favourable than compounds of carbon. There are three popular ways of making CNTs. Arc-discharge were the first way to produce the CNTs [38] it is a method where a high current is passed through two carbon electrodes placed in a gas (He, Ar or CH_4) atmosphere at low pressure. The nanotubes will form on the negative carbon electrode. Another way of producing CNTs is by laser ablation [39]. A metal-graphite target was heated by a laser. The evaporated carbon soot was transported to a cooled copper collector where the carbon nanotubes were formed. Both methods give CNTs that are bundled together and includes impurities such as amorphous carbon. Therefore the CNTs need to be separated and purified before they can be placed at the site of interest.

The third way of producing carbon nanotubes are by Chemical Vapor Deposition (CVD), where a carbon containing gas is used as a source for carbon atoms. Metal particles are used as catalysts for the growth that is further enhanced by heat and a plasma in a plasma enhanced CVD [40] The huge advantage of the CVD method over arc-discharge and laser ablation is that in CVD it is possible to place the catalyst particles on a substrate and then afterwards grow the CNTs exactly were they are wanted, without the same need for purification and manipulation. The catalyst particles are placed prior to the growth. The CVD growth method needs catalyst particles at the spot where the CNTs are to be grown. Transition metals (Ni, Fe, Co and Mo) are used as catalysts, the catalyst is defined using standard photolithography, and just before the CNT growth the chip is annealed at high temperature in order for the catalyst to form small islands the catalyst particle size and the CNT diameter is correlated**.** Figure 2.1. Shows all three methods of CNTs synthesis systems while Figure 2.2. shows the real CVD system used in laboratory and also grown sample of CNTs in Lab. Depending of the catalyst's adhesion to the substrate the CNT will stick to the surface and the CNT will grow from that (base growth) or the catalyst particle will be lifted from the surface and the CNT will grow under it (tip growth). Both ways of CNT growth are sketched in Figure 2.3.

2.2.2 Purification of CNTs

Nanotube synthesis produces nanotubes; however, the precise quantities of produced nanotubes depend on the method used and the exact experimental conditions [41]. Typically, a carbon powder generated during synthesis (as-produced nanotubes) can contain as much as 70-80 wt% nanotubes or as little as 10-15 wt% nanotubes. As-produced nanotubes are close ended and are often found mixed with materials that are unavoidable by-products of the manufacturing process [42]. Most common impurities

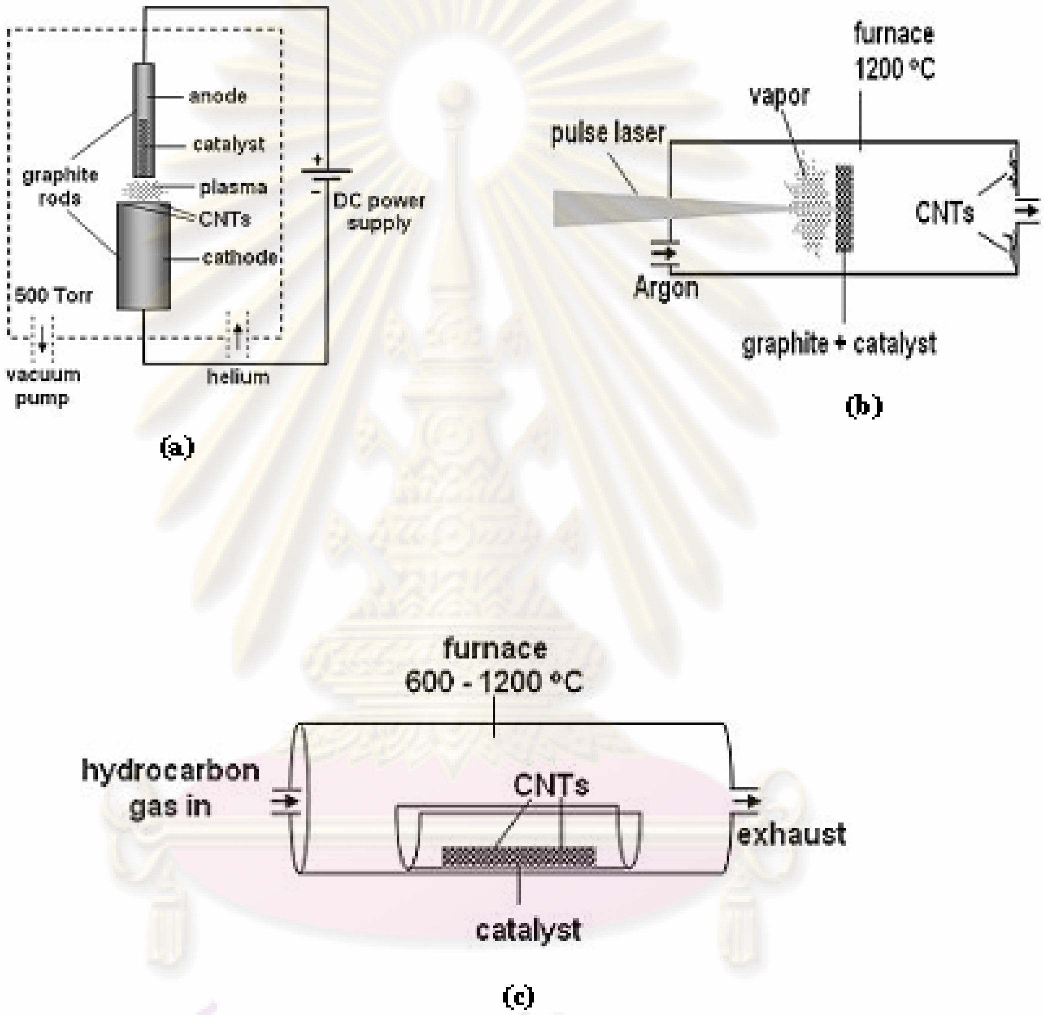
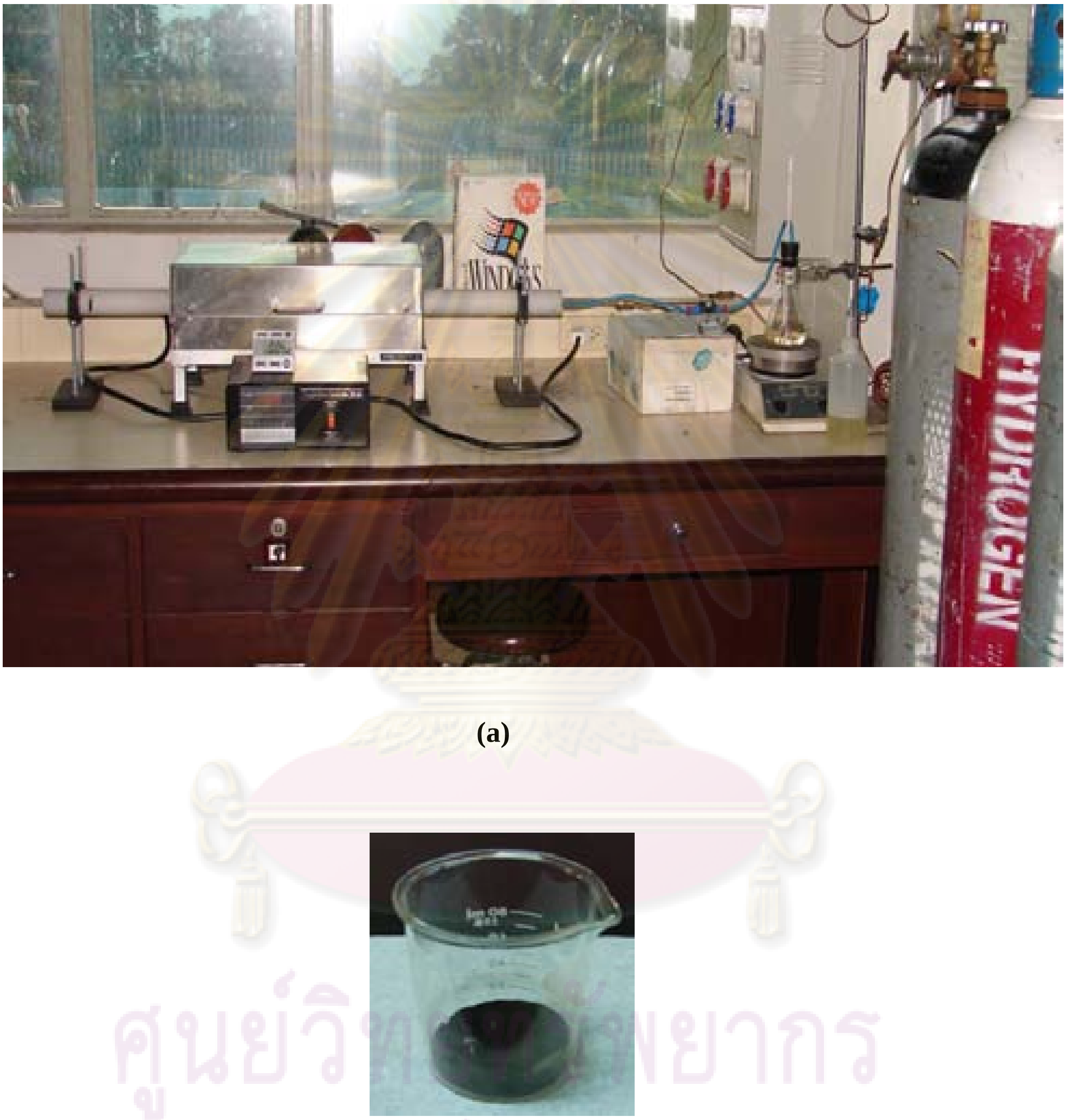


Figure 2.1 Carbon nanotubes synthesis systems (a) Arc discharge, (b) Laser ablation and (c) Chemical vapor deposition (CVD).


(a)

(b)

Figure 2.2 **(a) Real chemical vapor deposition (CVD) systems used in Lab. (b) sample of CNTs grown in Lab.**

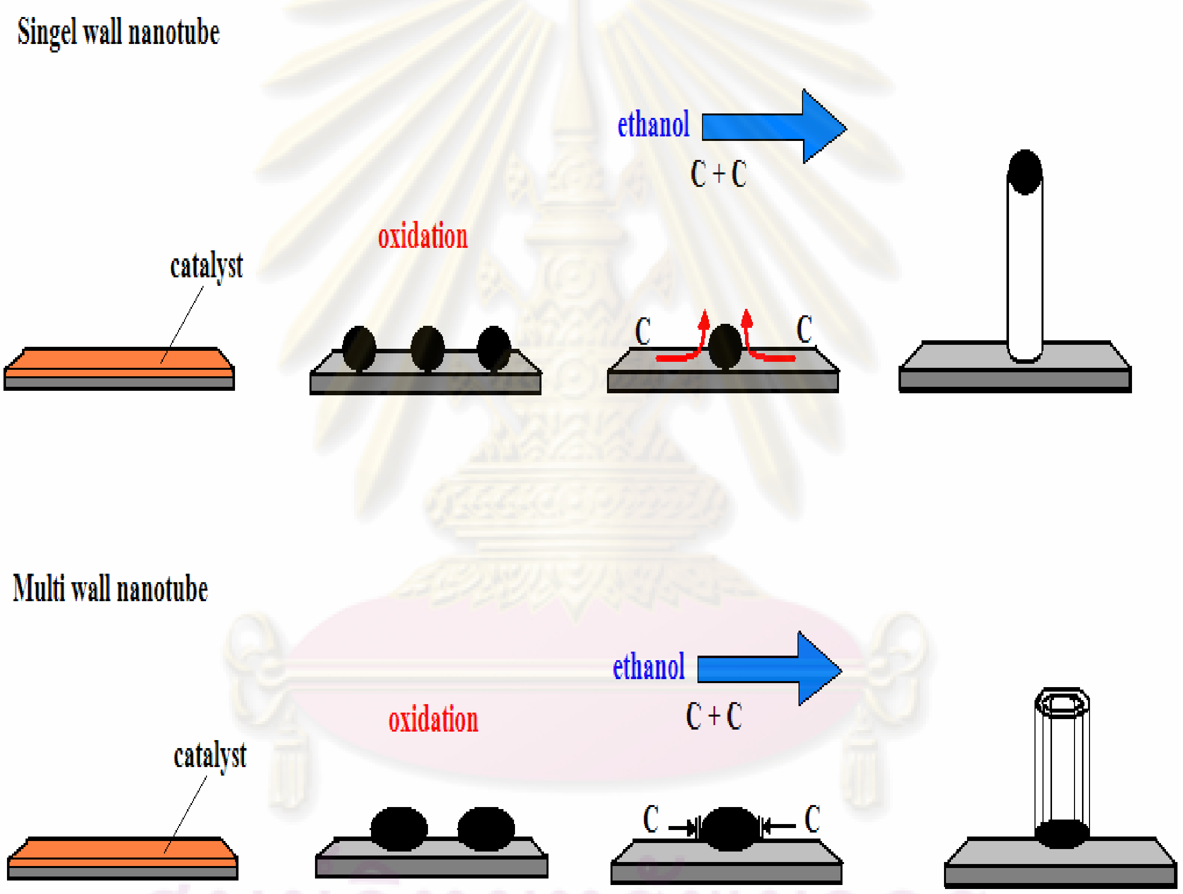


Figure 2.3 Growth of single wall and Multiwall carbon nanotubes.

are carbon coated catalyst particles, carbon nanoparticles or soot, and graphitic and amorphous carbons. Pure nanotubes can be extracted from as-produced materials by refluxing as grown nanotubes in acid for an extended period of time, which dissolves graphitic and metal particles. Heating as grown material in an oxygen rich environment to purify nanotubes can oxidize the graphitic and amorphous carbon, but is also known to remove some of the nanotubes.

2.2.3 Environmental applications of CNTs

The excellent mechanical, electronic and chemical properties of carbon nanotubes have stimulated some work by environmental scientists and engineers. Most work until now has been performed on the laboratory scale. So far, there are three main environmental applications of nanotubes, i.e. energy storage, sorbents and sensors. CNTs have potential to be used to develop new, “green” processing technologies that minimize or eliminate the use of toxic materials and the generation of undesirable byproducts and waste streams. However, the present cost of nanotubes, at hundreds of dollars per gram, limits large-scale applications of nanotubes in the near future. Although currently expensive, CNTs are also considered promising materials for hydrogen storage, an application that will be crucial in the development of efficient hydrogen-based vehicles [43] The reversible storage of hydrogen on nanotubes has attracted much attention from the energy and environmental protection field. Using hydrogen as an alternative energy carrier is rapidly developing due to an increasing demand for renewable and environmentally friendly energy sources [44]. It is reported that crystalline CNTs have a capacity for hydrogen sorption of 5-10 wt. % at pressures less than 1 bar near room temperature [45]. Such a hydrogen storage capacity would be a significant advance for the use of hydrogen as a fuel as high gravimetric density of hydrogen is a figure of merit. Extensive exploration of hydrogen storage has been performed by several research groups. However, the claimed hydrogen uptake capacity varied from less than 0.5% up to 10%. However, the uniform pore size distribution, high surface area and excellent electronic properties make nanotubes promising materials for hydrogen storage. Storage of other fuels in nanotubes also has been studied. Natural gas (methane is the primary constituent) adsorbed on porous materials is a promising alternative to compressed natural gas as a clean vehicular fuel, and for bulk transportation [46-47].

2.2.4 Adsorption on CNTs

It is understood that identifying the concepts of adsorption on carbon nanotubes would be the most important aspect to determine their significance to the environment. Adsorption can be of two types: chemical and physical. Chemical adsorption is essentially a chemical reaction involving formation of covalent bonds between adsorbate molecules and the atoms that comprise the surface of adsorbent. Physical adsorption, on the other hand, is caused by interactions due to van der waals forces and weak electrostatic forces between the adsorbate molecules and the surface atoms of the adsorbent [48].

The concepts of adsorption on carbon nanotubes are defined for physical adsorption. The unique cage-like structure of carbon nanotubes encloses a large hollow space, as a result nanotubes provide at least two adsorption surfaces: inside and outside. The inside surface of nanotubes can be accessed only when the nanotubes are open. The outside surface, however, is available unconditionally. The combination of inner and outer surfaces gives rise to a likelihood of various adsorption sites for CNTs. The probable adsorption sites for CNTs are: the inside surface of the innermost nanotube, concentric channels between nanotubes and the outer surface of the outermost nanotube shell. Moreover, concentric channels between nanotubes are believed to be accessible to a majority of adsorbate molecules [49].

Analytically, adsorption properties of a nanotube sample depend on three factors: degree to which nanotubes are open, contribution of individual adsorption sites, and sample purity. Operating nanotubes to various heat treatment processes can open the nanotubes; however, the number of open-ended nanotubes could vary from bundle to bundle. The role of adsorption sites can also be affected by surface defects and structural deformations on the nanotubes. The purity of a nanotube sample (i.e. wt% of nanotubes) is another important aspect of adsorption on nanotubes. This is because nanotubes are often found mixed with impurities, such as catalyst particles, soot and other forms of carbons, which could be highly adsorbent materials on their own and avoiding their presence could grossly misrepresent adsorption properties of carbon nanotubes**.** CNTs as sorbent in for organic analysis are summarized in Table 2.

Table 2.2 CNTs as sorbent for organic chemicals analysis

Type of CNTs	**CNT-format**	**Sample**	**Chemical Analytes**	**Analytical instrumentation**
SWNT	Packed tubing	Air	VOCs	GC-FID
MWNT	Packed column	Air	VOCs	GC-FID
MWNT	Cartridge	Water	Herbicides	HPLC-UV
MWNT	Micro column	Water	Acidic herbicide	HPLC-UV
Oxidize CNTs	Filter pads	Smoke	Nicotine and tar	GC-MS
SWNT	Glass bottle	water	Xylene	GC-FID
MWNT	Cartridge	Pork	Benzodiazepines	GC-MS
MWNT	Packed column	Eggs and pork	Sulfonamides	HPLC-UV
MWNT	Cartridge	Pork	Barbiturates	GC-MS
MWNT	Cartridge	Water	Dichlorodipheyl trichloroethane	HPLC-UV

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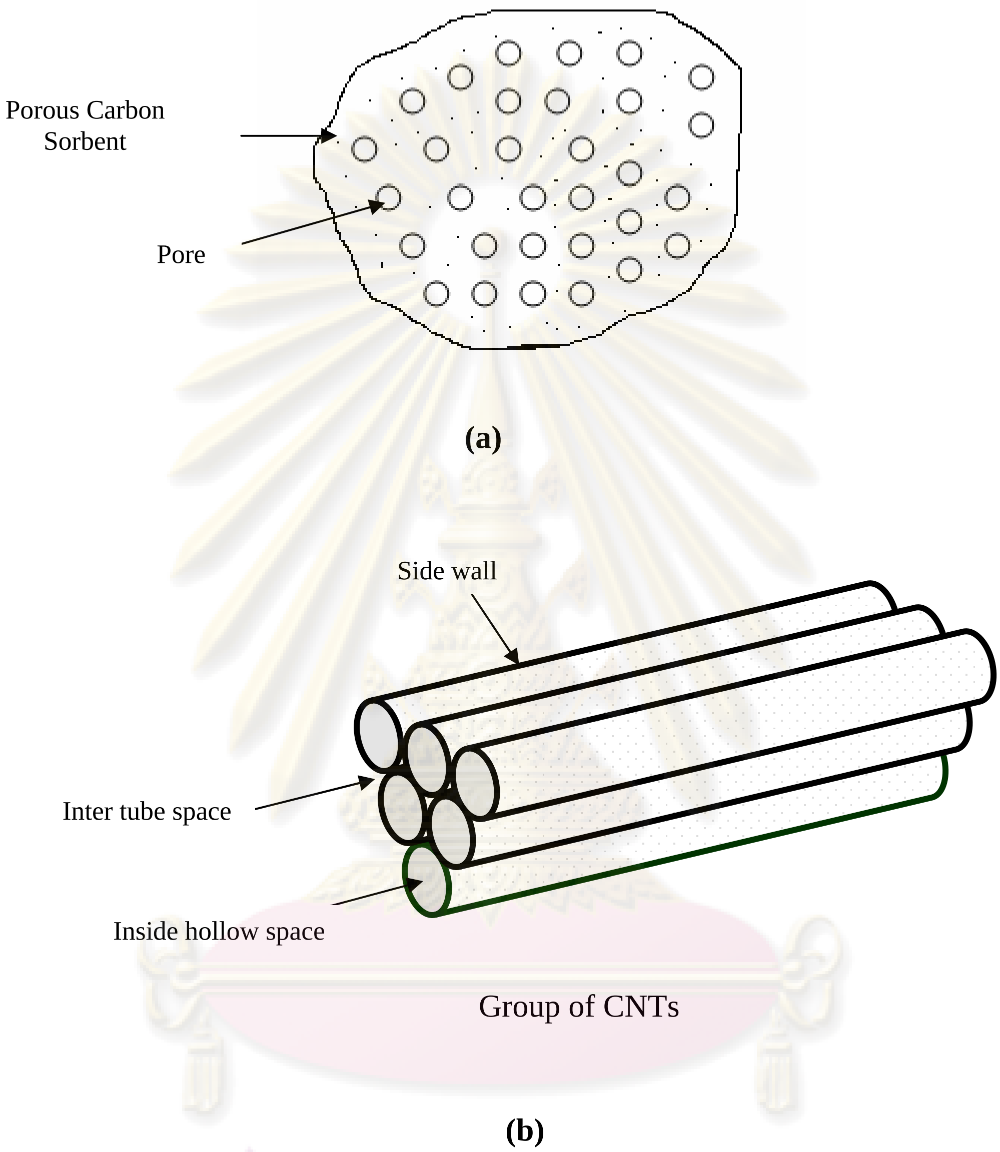


Figure 2.4 (a) Sketch of a porous carbon sorbent, (b) Carbon nanotubes with available spaces for sorption

Difference between porous carbon sorbent and CNTs in terms of available spaces for sorption are Sketched in Figure 2.4.

2.3 Instrumentation for characterization of CNTs

2.3.1 Scanning Electron Microscopy (SEM)

CNT nano-structured materials have at least one dimension smaller than 100 nanometers, which makes their characterization complicated and requires sophisticated instruments like Scanning Electron Microscopy. The morphology of CNT, their dimensions, and orientation can be easily revealed using Scanning Electron Microscopes with high resolution The use of SEM does not need preparation of the samples using a conductive coating. A Scanning electron microscopy (SEM) using Genesis 4000 XMS, EDAX Inc. (Mahwah, NJ, USA) has been employed in this study. A Shottky hot-field emission tip is employed as an electron source and has an ultimate resolution of 1.2-1.5 nm. A large specimen chamber housing a motorized stage with an internal CCD camera allows observation of fairly large specimens. The SEM chamber can be operated at a pressure of 1 to 20 Torr. Gaseous detection systems are used in imaging the samples. Partial ionization of the gas causes charge neutralization at the sample surface, with the oppositely charged species being collected by the gaseous secondary detector through a cascade effect. The overall outcome is an improved image of samples regardless of the nature of the samples [50].

SEM is a perfect technique to reveal the orientation of the CNT and to distinguish between the random type and aligned CNT arrays. The samples are normally directly mounted onto a standard aluminum fixture using double sided carbon adhesive tape. No further sample preparation or metallization is required, allowing the nanotubes to be imaged in their natural condition. The following set of parameters is used to obtain high resolution images of CNT, accelerating voltage of 10-20 KV, and a chamber pressure between 0.9-1.3 Torr.

2.3.2 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a technique that uses electrons rather than light to form an image of a sample. Optical microscopes are limited to a resolution of 0.2 µm, which is dictated by the wavelength of visible light. Electron microscopes, on the other hand, can have very high resolution (i.e., closely spaced features can be observed with great details) as the wavelength of an electron beam can be manipulated by the application of energy. In a TEM, an electron source produces high-energy electrons that are focused on a sample by various electromagnets, which accelerate and deflect electrons into an intense narrow beam. The sample is usually thin enough to be partially transparent to electrons. The electron beam interacts with the specimen, and gets diffracted in accordance with the physical features of the sample. The diffracted electrons cast a shadow of the specimen, which is viewed or recorded as an image on a film or on a computer [51].

TEM is a widely used technique to visually characterize the structure and type of carbon nanotubes. It can also be used for a qualitative estimate of sample purity i.e., to determine the presence of non-nanotube structures. In this study, the nanotube samples were analyzed by using a transmission electron microscope (TEM) from Topcon Corp. (Tokyo, Japan).that is available at NJIT. This electron microscope utilizes a 200 kV electron source and has a resolution of 2.8 Å. The samples for TEM analysis were prepared by the standard procedure of dissolution in > 99% pure acetone followed by an hour of sonication (Cole Parmer Ultrasonic Cleaner 8892). A drop of acetone-SWNT solution was placed on a carbon holey grid and was dried in air. The carbon holey grid was mounted on a TEM sample holder and was then analyzed for the presence of carbon nanotubes.

2.3.3 Thermogravimetric techniques (TGA)

Thermogravimetric techniques were used to characterize the thermal stability (i.e. ability to withstand high temperatures without combustion) of CNTs. Thermogravimetry is the measure of change in sample weight as a function of temperature. This technique can characterize materials that exhibit weight loss or gain due to mechanisms such as decomposition, volatilization and oxidation [52]. The thermal analysis of CNT samples was performed using a Thermogravimetric analyzer of Q500 TGA from TA Instruments (New Castle, DE, USA). This system is capable of measuring weight changes of samples up to 100 g with a sensitivity of 1 µg from room temperature to 1,000 ^{o}C. In a typical run, a sample (4 - 10 mg) was placed in a platinum sample pan that was suspended in a quartz tube that was enclosed in a vertical electric furnace. A gas flow (100mLmin^{-1}) of research grade air was maintained over the sample to carry the combustion products to the reactor outlet. The furnace was heated from room temperature to up to 900 ^{o}C at a constant temperature ramp of 1 ^{o}Cmin^{-1}. At 900 ^{o}C, the furnace temperature was held constant for 10 - 15 min to stabilize the fluctuations in sample weight due to temperature changes. Computer acquired time, weight and temperature data at an interval of 10 s. The buoyancy effects (changes in gas density with increase in temperature) were circumvented by operating the TGA with an empty sample pan under similar operating conditions.

2.3.4 Fourier Transform Infrared spectroscopy (FTIR)

Fourier Transform Infrared (FT-IR) is an analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic. It is used to identify unknown materials and material phases present in a specimen [53].

The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies that are characteristic to that molecule. During FT-IR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FT-IR spectral pattern is then analyzed and matched with known signatures of identified materials in the FT-IR library. The Fourier Transform Infrared spectroscopy (FTIR) measurements of functionalized CNTs were carried out in purified KBr pellets using a PerkinElmer Spectrum One instrument (Downers Grove, IL, USA). The measurements were taken in the range of 450-1100 cm^{-1} with 32 scans performed per sample. Data were analyzed by visually comparing observed differences in intensity of characteristic peaks.

2.4 Characteristics of Adsorption and Desorption for microtrap

2.4.1 Adsorption

Adsorption is a physical process that deals specifically with the concentration of dispersed material in a continuous phase (carrier stream) on the surface of a highly porous material. There have been many complex theoretical approaches taken to explain the adsorption phenomenon. Adsorption is not only a function of physical parameters such as temperature and pressure, but also of concentration and inter-molecular interaction. To put the problem into a simple framework, the theories are presented on a broad basis that will hold true for most materials and conditions. It can be stated, therefore, that the amount of a given gas adsorbed at equilibrium is a function of the final pressure and temperature only [54]

The adsorbent must satisfy a number of requirements, such as total chemical inertness relative to the adsorbed compounds, a capacity for total desorption and an adsorption capacity as large as possible for a maximum number of compounds. Two of the most critical parameters for an adsorbent are breakthrough volume (BTV) and desorption efficiency [55].

2.4.2 Breakthrough volume (BTV)

Breakthrough volume (BTV) is defined as the volume of carrier gas per unit mass of adsorbent necessary to cause a mass of adsorbate molecules, introduced into the front of the sorbent tube to migrate to the back of the tube. The BTV is also defined as the sampled volume corresponding to the end of the linear domain. The extreme value of the linear domain is evaluated by calculation of the intersection between linear and non-linear domains. The preconcentration of a compound on an adsorbent can only be quantitative at sampling volumes that do not exceed the BTV of the compound. Earlier studies suggested an empirical equation to estimate the breakthrough regarding the boiling point of the adsorbate [56]. It has been demonstrated that the BTV depends on numerous factors such as humidity, temperature and concentration of adsorbate. There are also some other parameters which may affect the BTV value such as the chemical composition of the gaseous mixture [4], the flow-rate and linear velocity of the carrier gas [6], the dimensions of the trap [7]. A number of parameters relating to the adsorbent can also effect BTV, such as mass, granutometry, pore diameter and specific surface area, repeated re-use and thermal pretreatment.

When considering the effect of humidity, it is necessary to take into account the change in the adsorption due to the interactions of the substance with the adsorbed water itself. Hydrophobic, non-polar porous polymers adsorb small amounts of water, and the effect of water vapor on these materials is insignificant. As the moisture content of the air increases, cooperative interactions between water molecules take place on the surface and render it hydrophilic, causing a dramatic drop in capacity for hydrophobic organic molecules. The breakthrough study on Anasorb CMS showed the adsorbed methylene chloride did not appear to be lost at high humidity, and in this case breakthrough can be attributed solely to saturation. The organic and the moisture molecular can coexist as a mixed phase in the pore structure of a molecular sieve carbon, the composition of the mixed phase being related to the composition of the atmosphere with which it is in equilibrium [9].

Temperature is another important parameter influencing breakthrough [18-20]. Adsorption is an exothermic phenomenon, the BTV being related to the temperature by Van't Hoff-type relationship:

$$\frac{d[\log(BTV)]}{d(\frac{1}{T})} = -\frac{\Delta H_{ad}}{2.3R}$$

Where ΔH_{ad} is the adsorption enthalpy, R is the gas constant and T is the absolute temperature. This equation can be expressed as

$$\log(BTV) = a + \frac{b}{T}$$

Using the equation the BTV can be estimated at a given temperature. The BTV is also a function of concentration. Normally, the BTV data were obtained at infinite dilution (i.e., the extreme lower end of the Henry's Law region) and thus represent a migration volume rather than a saturation, or capacity, volume. This region of adsorbate coverage is applicable to sample enrichment modes for which trace level analyses are required. Under this circumstance, the concentration of adsorbate was always neglected when BTV was discussed [4-7].

However, sorbent traps used for air sampling are usually short and do not have as many theoretical plates as an analytical GC column. There are several reasons why the use of short columns is advantageous. They have low pressure drops and do not require complicated pumping equipment. This is especially true for field sampling. A high flow rate is often desired, as it permits the collection of a large volume sample. A small physical size is also advantageous in the desorption step. The sample enters the trap as a front instead of a narrow plug, as no separation is intended. For this short, low plate number sampling trap, the concentration effect on the front shape of the elution peak can not be neglected [22, 24, 26]. The numerical solution expressed was found to be a good approximation of breakthrough volume as a function of plate number:

$$BTV = V_R\left(a_0 + \frac{a_1}{n} + \frac{a_2}{n^2}\right)^{-1/2}$$

where V_R is retention volume, n is theoretical plate number, a_o, a_1 and a_2 are constants related to breakthrough level.

2.4.3 Measurement of Breakthrough

Breakthrough is measured by three different methods [1,4]. The first is to measure response for the microtrap pulse as a function of injection interval. Increasing the interval time increases the response as more samples are accumulated by the microtrap. Once the sample begins to breakthrough, the response does not increase anymore because no further sample accumulation occurs. The breakthrough can be found at the maximum response. The breakthrough time corresponds to the time which the maximum response is reached as shown in Figure 2.5 (a)

The second method uses the peak shape of the microtrap injections as the sample flows continuously through. When the microtrap is heated, a desorption peak occurs. As the sample flows continuously, the analytes are re-adsorbed in the microtrap. This lowers the base line into the negative territory appearing as a negative peak. As-sample begins to breakthrough, the detector response increases and the response increases again. The horizontal line shows region where microtrap passes the breakthrough point. The width of the negative peak at the base line equals the breakthrough time as shown in Figure 2.5 (b).

The conventional method is using frontal chromatography as shown in Figure 2.5 (c). When a sample stream containing organics is introduced, initially the response stays constant and then as the sample front breakthroughs, the response increases to a steady value. Here the breakthrough volume is calculated based on the time required for breakthrough. For this study, the first method was chosen because it was the operationally simplest method.

2.4.4 Desorption

Complete desorption of the adsorbed organics from the adsorbent is also critical for quantitative analysis. If an analyte is adsorbed on a very strong adsorbent, it may not be efficiently released during the desorption process. Also, analytes subject to thermal breakdown can not be held at high temperatures too long. Both of these occurrences can lead to poor recovery of the analyte. Desorption efficiency of several Organics have been studied [7,24-25] a symmetrical desorption peak, the maximum volume of carrier gas required for complete desorption is reported to be twice the retention volume.

2.4.5 Adsorption/ Desorption on non porous structure

Adsorption on non porous structure is different than porous structure as sorption is mainly happened on the surface of sorbent due to physical attractions. The desorption profiles of the analytes from the sorbent can be used as basis to understand structure of the sorbent i.e., porous or non porous. As CNTs are nano scaled tubes but in most of the cases these are closed ended, accordingly, most of the sorption happened on their tubular surface and interstitial spaces between tubes. As a result the sorption of organic compounds to CNTs were mostly reported to be a process of physical interaction and without charge transfer between the adsorbates and their hosts [37,45]. Several studies confirmed the presence of π-π interactions for the sorption of aromatics to CNTs [48,46,52]. Such interactions are supportive of the concept that sorption on CNTs mainly on their surface of nanotubes and not within their hollow spaces. Nevertheless, research in this area is still fragmentary and not complete enough for making clear conclusions.

Organic compounds adsorption on CNTs is comparable to or even higher than that on other form of carbons. Thus, surface area and tubular structure may be a direct parameter to predict organic analyte-CNT interactions. Generally, π-π interactions depend on the size and shape of the aromatic system and the substitution unit. An increasing number of theoretical (calculation or simulation) studies indicated that the π-π interactions between CNTs and aromatic adsorbates and thus increase the possibility that CNTs are non porous in nature [48-49]. Therefore, in this study CNTs are considered as non porous structure whereas commercial Carbopack^{TM} is a porous structure sorbent.

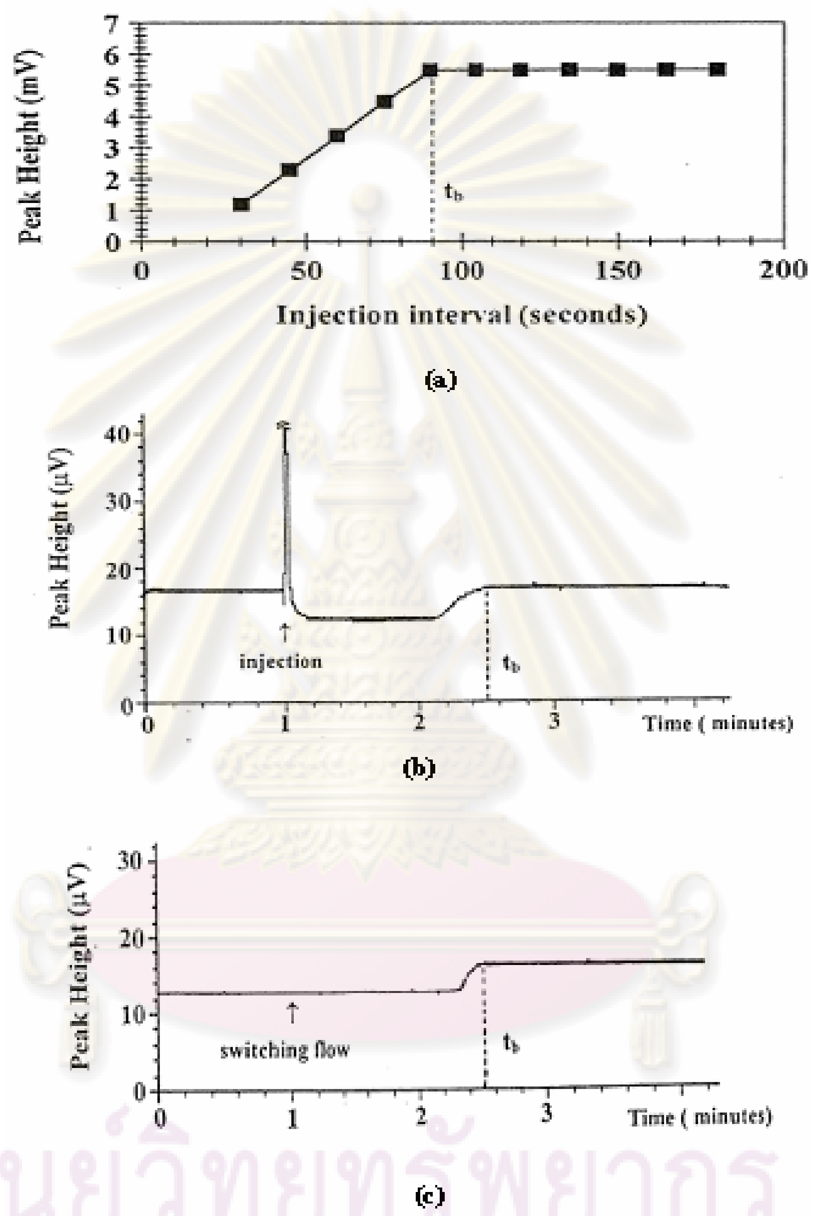


Figure 2.5 **Breakthrough time by different methods (a) Response of the analytical system as function of interval between microtrap pulses (b) Characteristics peak from a microtrap (c) chromatogram generated by frontal chromatography**

CHAPTER III

MICROTRAPPING OF VOLATLIE ORGANIC COMPOUNDS WITH CARBON NANTOUBES

3.1 Introduction

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 rolled up of a single and multi layers of graphene sheets respectively [57].

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. 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 walls type forces. This eliminates the mass transfer resistance related to the 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. Based on what has been reported, both retention and desorption are highly favorable on CNTs. They have the potential to be the next generation, high performance sorbents for both volatile and semi volatile organics [58].

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 a different trapping mechanism that can be diffusion controlled. So, purity of the CNTs is an important factor that influences the overall effectiveness as a sorbent [59].

The sorption sites on CNTs are on the wall, and in the interstitial spaces between tubes. These sites are easily accessed for both adsorption and rapid desorption. The NTC coverage on the CNT reduces their availability, as the sorbate has to diffuse through the NTC to reach the CNT. Moreover, the porous structure of NTC introduces mass transfer limitations, slowing both adsorption and desorption. Understanding these characteristics is important for their application separation media [60].

The excellent features of CNTs, along with their nano-scale features, make them ideal candidates for micro-scale devices, such as, a micro-concentrator or a micro-sorbent trap, which have been used in a variety of chromatography and sensing applications. The purpose of such devices is usually to act as fast preconcentrator or to modulate the concentration of a stream for real-time monitoring. They have been fabricated in small capillary tubings and also by micromachining silicon and other substrates [1, 61].

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 accumulated inside, thus, making it prone to breakthrough. For quantitative sampling, the sample volume should not exceed its breakthrough volume defined as the volume that can be sampled per unit weight of the sorbent before the analyte is lost. 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 /min before rapid desorption [4,7,22,55]. 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.

The objective of this chapter is to study the sorption of select volatile organic compounds on SWNT, MWNT and self-assembled CNTs. The goal is to study these sorbents on a comparative basis, and evaluate their effectiveness as analytical sorbents. The other objective is to evaluate their applicability in a micro-sorbent trap.

3.2 Experimental

3.2.1 Materials

A MWNT sample synthesized by CVD using ethanol as a precursor and Ni as catalyst was obtained from Chaing Mai University [62]. This sample, which had not been standardized contained significant NTC is referred to as MWNT-1. In an effort to eliminate the NTC and purify the CNTs, first the sample was passed through 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^{o}C for 30 min. The cleaned MWNT-1 was referred as MWNT-1C. Purified SWNT and MWNT (referred MWNT-2) were purchased from Cheap Tubes Inc., Carbopack^{TM}, which was purchased from Supelco Inc. was used as a basis for comparison.

3.2.2 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 [63]. First the steel tubing was heated in air a 10 mL/min flow at 500^{o}C for 30 min to oxidize the surface. Then the surface was reduced in a 10 mL/min flow of H_2 at 500^{o}C for 30 min. The oxidation and reduction led to the formation of a catalytically active surface. After this, chemical vapor deposition (CVD) was carried out at 700^{o}C for 1 hr. using C_2H_4 as the precursor. To remove the NTC from CNT surface, a thermal annealing in the presence of oxygen was carried out at 350^{o}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).

3.2.3 Experimental System

The experimental system is as shown in the Figure 3.1. Parts per million level organic compound standards were generated using a diffusion tube method reported before [64]. The N_2 stream containing the organic compounds flowed through the microtrap continuously and 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 1-1.5seconds, 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 a 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.

3.3 Results and discussion

3.3.1 Purifications of CNTs

Figure 3.2(a), shows the SEM image of MWNT-1, which appears to be covered with NTC. Some of it comprised of 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 3.2(b) is the SEM of MWNT-1C, which had been cleaned by sieving to remove the large particles, and then by oxidation in air at 350 ^{o}C to eliminate the amorphous carbon on the surface. This preparation showed mainly CNTs with some residual NTC. Too long an 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 Figure 3.2(c), 3.2(d) respectively, which show relatively pure preparations that did not require any preprocessing. The length of the CNTs ranged from a few hundred nanometers to micrometers while the average diameter ranged of 10–20 nm for SWNT and 20–40 nm for MWNTs respectively.

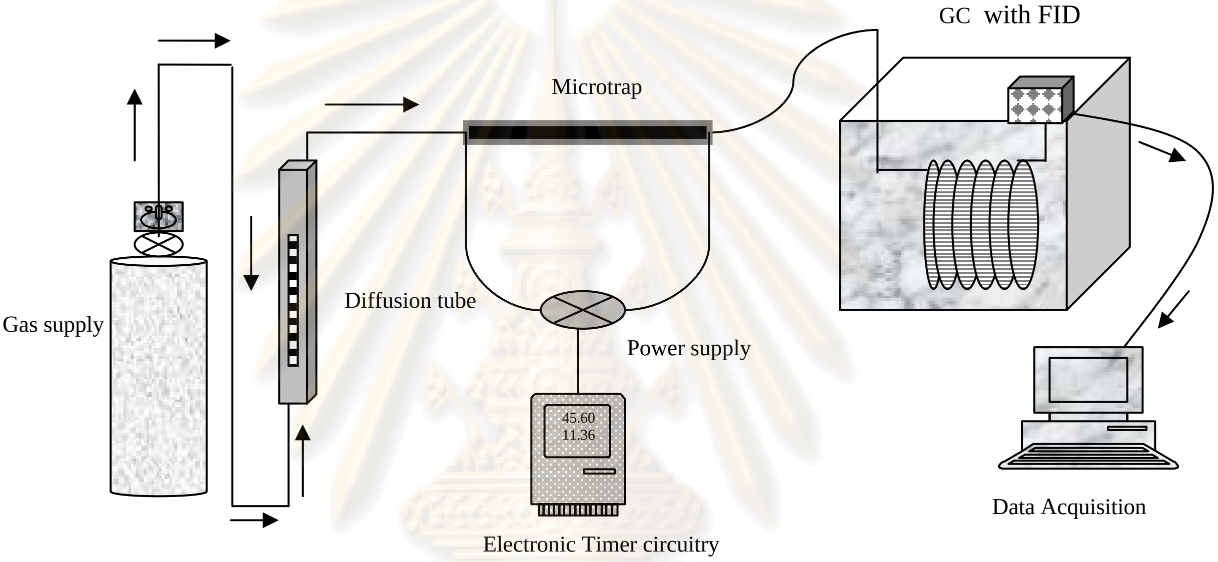
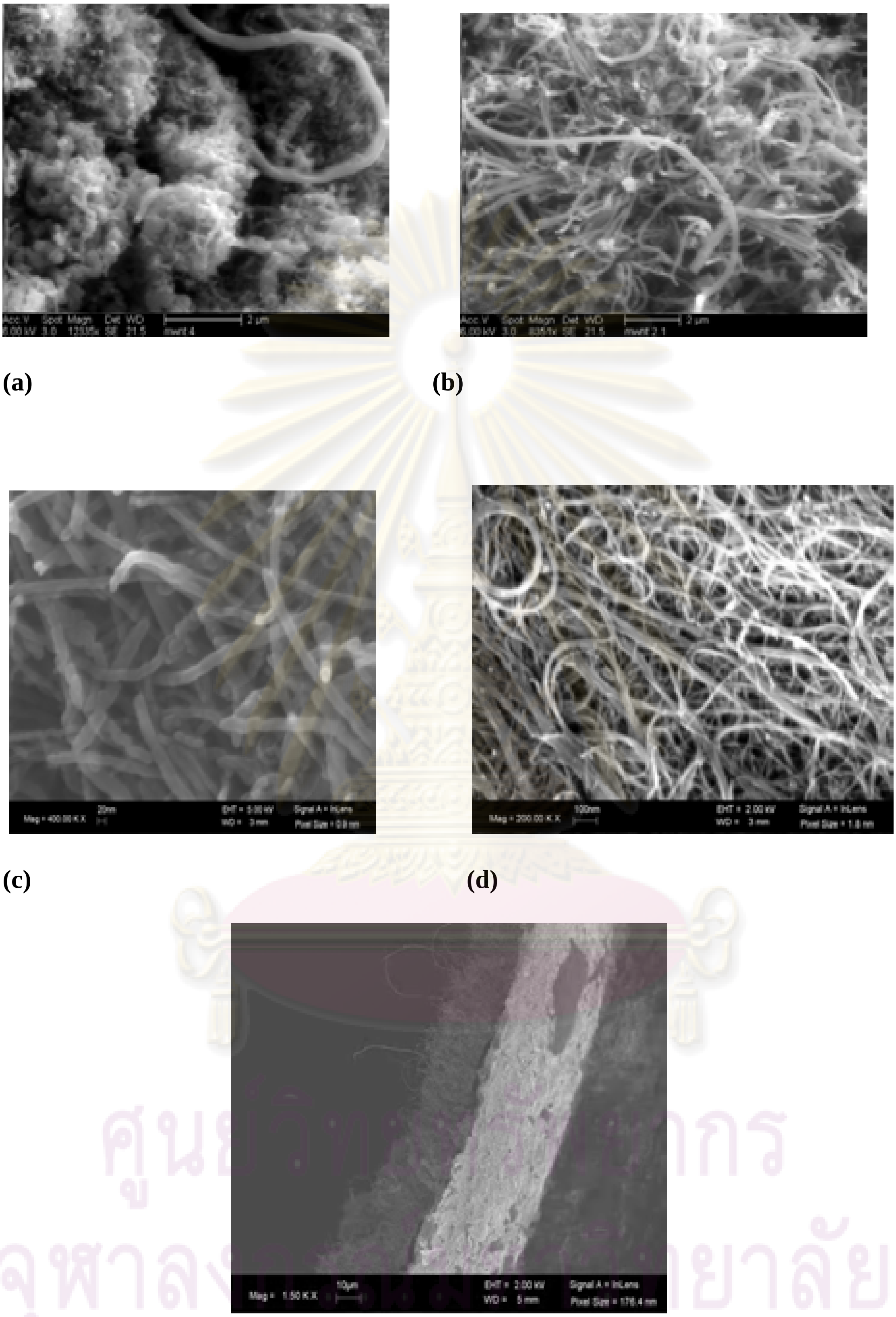


Figure 3.1 **Schematic diagram of the experimental system**.



(a) (b)

(c) (d)

(e)

Figure 3.2 SEM images of; (a) MWNT-1, (b) MWNT-1C, (c) MWNT-2, (d) SWNT and (e) self-assembled CNTs.

Figure 3.2(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^{o}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 MWNT-1C. The film thickness of self-assembled CNTs was found to be about 20 µm, and they were uniformly distributed through out the microtrap.

The characteristics of the different CNTs in terms of their surface area, average diameter and length are presented in Table 1. SWNT while MWNT-2 had the highest BET (Brunauer, Emmett, and Teller) surface area that were significantly higher than CarbopackTM.

Table 3.1 Characteristics of the different carbon nanotubes used in the microtraps.

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

3.3.2 Breakthrough characteristics of the microtrap

As the N_2 continuously flowed through the microtrap, the organics 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 [4,19]. This is known to be a function of the capacity factor, length, and flow rate. The Breakthrough time 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 requires to reach the maximum response [24,56].

Five organic compounds represented a wide range of volatility with varying polarity were analyzed. Typical breakthrough profiles for SWNT are seen in Figure 3.3, with toluene showing the longest breakthrough time. Sorption on other CNTs were similar, and are not presented here for brevity. The comparison of different sorbents when it comes to the retention of toluene is shown in this Figure 3.4. For the same mass of sorbent, all the CNTs showed significant higher sorption capacity compared to Carbopack, the only non-nanotube 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 demonstrates 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 small quantity of CNTs.

Table 3.2 Breakthrough times (min) for different sorbents and analytes.

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

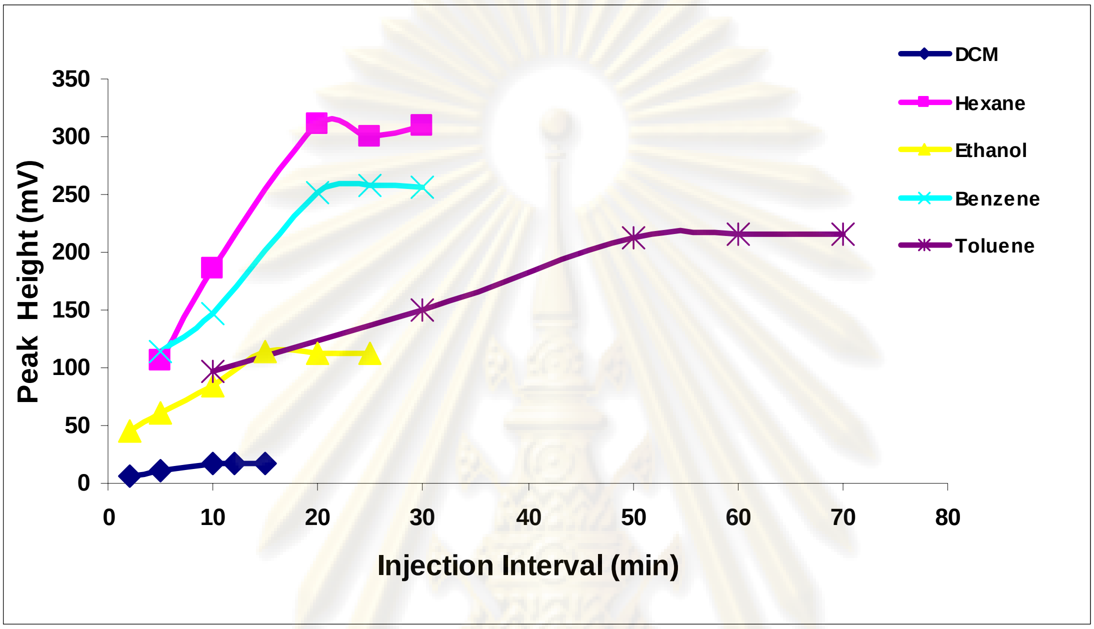


Figure 3.3 **Detector responses as a function of injection interval for the SWNT microtrap.**

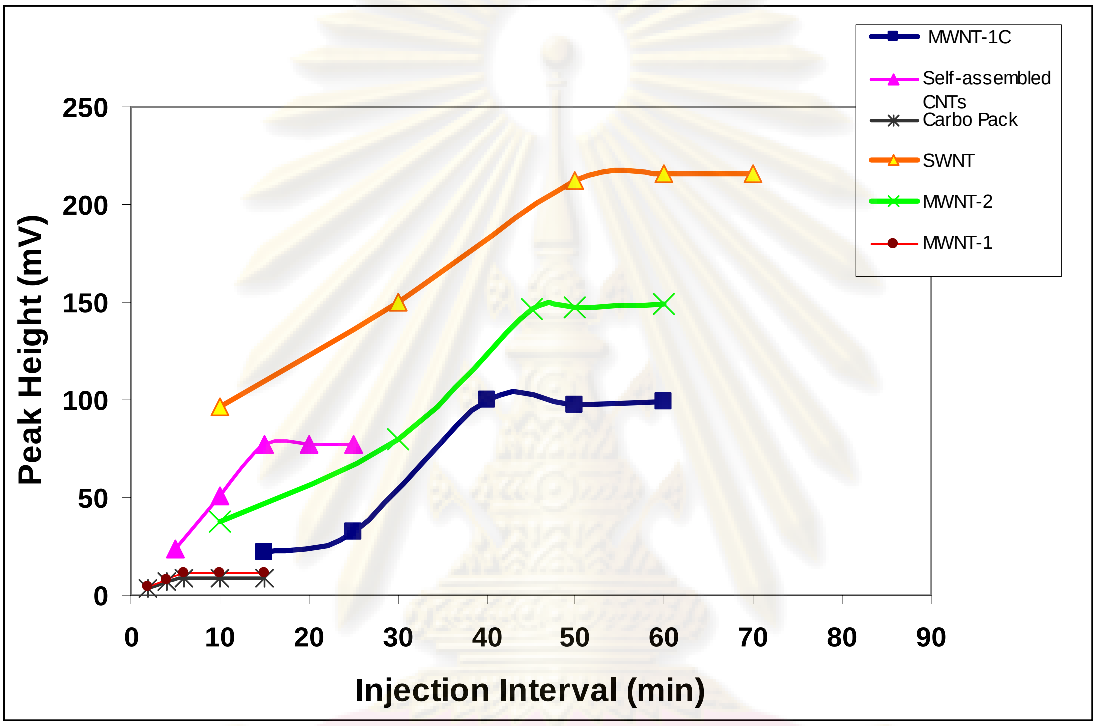


Figure 3.4 Detector response as a function of injection interval for toluene using microtraps containing different sorbents.

The breakthrough time for different compounds on the different sorbents are listed in Table 3.2. 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 time that were closer to MWNT-2, but were consistently lower. This was attributed to higher impurities in the former, 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 [61]. Although benzene and hexane exhibited similar breakthrough times, while xylene showed significantly longer breakthrough times. From Tables 3.1 and 3.2 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.

3.3.3 Breakthrough Time as a Function of Temperature

Adsorption is an exothermic phenomenon and the breakthrough time of a compound is inversely proportional to the temperature. As expected when adsorption temperature was decreased the breakthrough time increased. The results followed the Van’t Hoff-type relationship [65] as shown in Figure 5. The plot of Log BTV as a function of 1/T and was found to be linear according to:

$$\mathbf{Log\ (BTV) = k_1\ 1/T + k_2} \qquad \mathbf{(3.1)}$$

where, BTV is the breakthrough volume and k_1 and k_2 are constants. T is the absolute temperature. It was interesting to note that the slopes varied for the different sorbents with SWNT showing the highest while Carbopack the lowest.

The isosteric heat of adsorption, ΔH_s is the amount of heat released when an atom adsorbs on a substrate, and is related to the activation energy of sorption for a sorbate-sorbent system. The strength of interaction of compound with the surface of the of the adsorbent is represented by the enthalpy of adsorption, ΔH_s, given by [66]

$$\Delta H_s = -R \frac{\partial (\ln BTV)}{\partial (1/T)} \tag{3.2}$$

The ΔH_s were obtained from the slope of plots of ln BTV vs 1/T, where BTV is the breakthrough volume of the organic compound on the sorbent, T is the absolute temperature and R is the gas constant. A linear dependence indicated a constant value of the isosteric heat of adsorption in the temperature range studied, while relative change in ΔH_s of sorbents with temperature is attributable with the activation of the sorbent surface. These values for benzene are presented in Table 3.3. The maximum ΔH_s was for SWNT, suggesting that it had the strongest interaction with the analyte. This was followed by MWNT-2 and MWNT-1C. MWNT-1 and Carbopack showed similar values of $\Delta H_{s,}$ about a third that of SWNT. Once again this demonstrated that the mechanisms of adsorption were quite similar in these two sorbents. It is interesting to note that the ΔH_s followed a trend similar to that of the breakthrough times for the different analytes.

Table 3.3 Isosteric Heats of Adsorption (ΔHs) for different carbon nanotubes using benzene.

Sorbents	**ΔHs (k J/ mol)**
MWNT-1	18.49
MWNT-1C	44.92
MWNT-2	56.43
SWNT	63.91
Carbopack	18.155

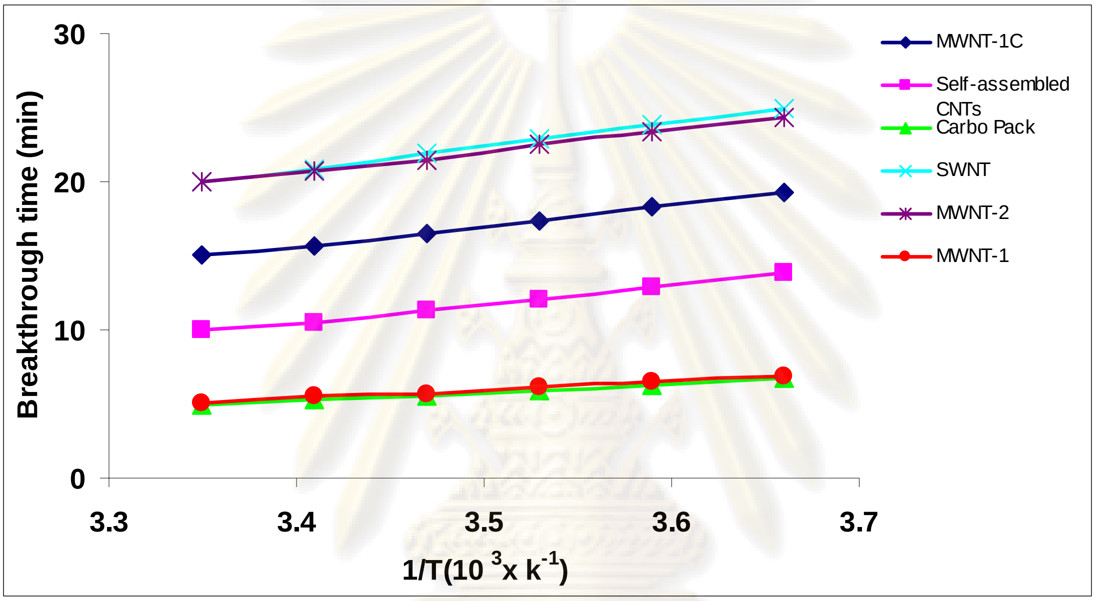


Figure 3.5 Breakthrough time as a function of 1/T. Benzene was used as the analyte.

3.3.4 Quantitative 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 quantitative desorption, enough energy need to be provided [26]. Figure 3.6, 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.

Table 3.4, 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 at 3 mL/min, the difference was 29%. However for benzene at a 6 mL/min, 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 excellent sorbents that 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.

Table 3.4 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/min
2. Flow rate of 6 mL/min

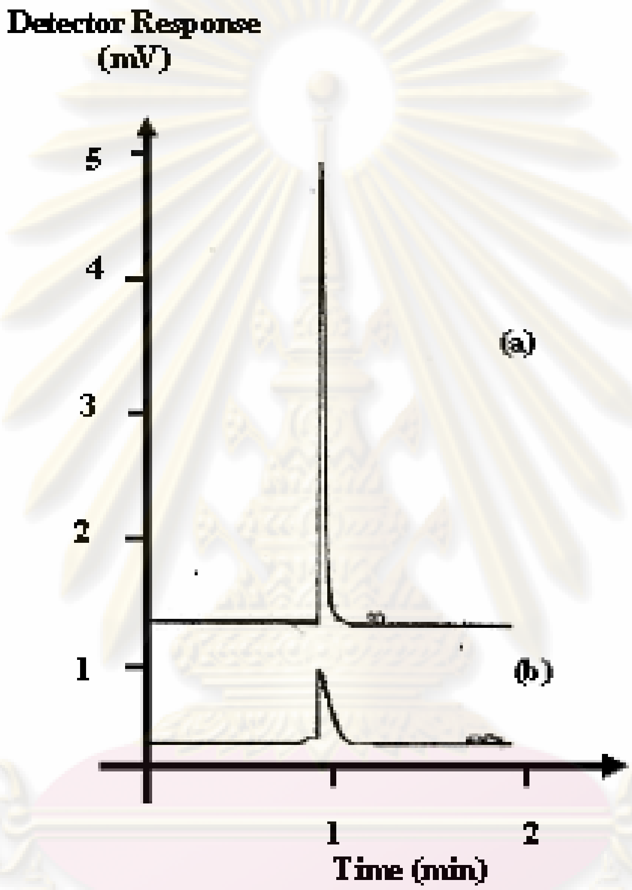


Figure 3.6 Desorption profile of toluene with different sorbents inside microtrap; (a) SWNT (b) Carbopack.

3.4 Conclusions

The data shows that the carbon nanotubes are highly favourable for both adsorption and desorption. The former is characterized by breakthrough volumes and isosteric heats of adsorption (Δ Hs) close to 64 kJ/mole as compared to 18 kJ/mole for a non-tubular carbon. Similarly, rapid desorption from CNTs was demonstrated by narrow desorption band width. The elimination of NTC from the CNT surface is important, as they reduce the performance of these sorbents.

CNTs packed and self-assembled CNTs inside microtrap interfaced with gas chromatography have been used to study the sorption and desorption of VOCs. The properties of contaminated MWNTs were successfully enhanced by selective removal of non-tubular carbons. The role of NTC material in the sorption of VOCs on CNTs is very important.

CHAPTER IV

MICROTRAPPING OF SEMI-VOLATILE ORGANICS WITH CARBON NANOTUBES

4.1 Introduction

Micro-sorbent traps referred to as a microtrap serve as integrated concentration-injection devices for continuous monitoring of gas streams. These have been fabricated from microbore capillary as well as via silicon micromachining. Their small dimension allow rapid desorption of adsorbed compounds, with potential advantages of faster operation, smaller bandwidth and low detection limit. Consequently they have been used in chemical sensing, trace monitoring, and in gas chromatography (GC). The sorbent selection for microtraps is of great importance because the analytes need to be retained in a small quantity of sorbent, and at the same time desorbed rapidly for fast, quantitative detection [67].

A single-walled carbon nanotube (SWNT) is formed by rolling up a graphene layer, while multi-walled carbon nanotubes (MWNT) consist of multiple concentric tubes. The carbon nanotubes (CNTs) have excellent mechanical strength, are thermally stable and exhibit high electrical as well as thermal conductivity. These features make them attractive to a wide range of applications ranging electronincs to polymer composites. The reported surface area of CNT are in the range of 150-500 m^2/g, which makes them attractive as sorbents. They have been used in pollution control to remove trace contaminants such as heavy metals, dioxin, 1,2-dichlorobenzene and trihalomethanes from air and water. They are also effective in sorbing small molecules like H_2, O_2 and methane, that would normally be retained by specialized molecular sieves. As a result, hydrogen storage via adsorption has been studied extensively for fuel cell application [33,43,48,68].

The CNTs themselves are nonporous structures. However, the opening of the tube-ends may generate internal pores inside the hollow tubes. The interstitial voids between the tubes may also act in a manner similar to pores. However, compared to conventional sorbents such as activated charcoal and Carbotrap, for all practical purposes the CNTs may be considered nonporous or relatively nonporous. This is one of the major advantages of CNTs, where the solute is held on the surface by van der walls type forces, thus eliminating the mass transfer resistance related to the diffusion into elaborate pore structures. The high capacity sorption of the CNTs comes from their large aspect ratio. In general, the two important issues in sorbent applications are high adsorption capacity and efficient desorption. The combination of non-porous structure and large surface to volume ratio lead to favorable conditions for both these phenomenon [31]. 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 small molecules to relatively large polycyclic aromatics. Their application in the sampling of volatile organics has been demonstrated [61,69], and if the range can be extended to relatively larger semi-volatile compounds, then they have the potential to be the next generation, high performance sorbents.

The synthesis of CNTs generally involves the catalytic dissociation of graphite, or chemical vapor deposition of organic precursors such as CO and ethylene. During these relatively uncontrolled processes other disordered and non tubular carbons (NTC) carbons are also formed [59]. Typically, the presence of a nano-structured catalyst leads to the formation of CNT, and once the catalyst becomes unavailable, NTC is formed. So, most CNTs preparations contain the latter in the form of a surface coating. The morphology of NTC are unpredictable, and they tend to have porous structures. They also have relatively high adsorption capacity somewhat similar to charcoal, where both sorption and desorption tend to be diffusion controlled. The diffusional resistance is particularly relevant for the larger semivolatile compounds. So, purity of the CNTs is an important factor that influences the overall effectiveness as a sorbent.

The sorption sites on pure CNTs are on the outside wall and in the interstitial spaces between the tubes. These sites are easily accessed by the solute during adsorption and desorption. The NTC coverage reduces this availability and provides an additional barrier through which the molecules have to permeate to reach the CNT; thus slowing the overall process and reducing its efficiency.

The breakthrough and desorption efficiency are important characteristics of a sorbent trap. For quantitative sampling, the total amount should not exceed its breakthrough volume (BTV) defined as the volume that can be sampled per unit weight of the sorbent before the analyte is lost. Based on previous reports [26,31], the semivolatile organics may be expected to have relatively large breakthrough volumes, however their desorption may be an important issue. Of particular interest to analytical community is the development of micro-scale devices, such as, a micro-concentrator or a micro-sorbent trap (referred to as the microtrap). These have been used in a variety of chromatography [6,8,13] and sensing applications [47-49]. The nano-scale features of CNT make them ideal candidates for assembly in small devices, whose purpose often is to act as fast acting pre-concentrators with high capacity [50-52]. They have been fabricated in small capillary tubings and also by micromachining silicon and other substrates [53-54].

The microtraps are designed to be of small diameter, so that they have large number of plates to prevent breakthrough and can be desorbed rapidly by direct resistive heating. Therefore, they contain small amounts of sorbent, often designed to retain the analytes only for a few seconds/minutes before rapid desorption [55]. Once, the breakthrough volume reaches a satisfactory level, desorption plays an important roles in a fast acting microtrap, and an understanding of this processes provides insight into the characteristics of these nano sorbents. The CNT phase can be packed into a microtrap [69,70], or self-assembled in an open tubular format with a few micron thick film [61,63,69,71]. The latter facilitates faster heat transfer, while the former contains a larger amount of the sorbent.

The objective of this chapter is to study the retention and effective desorption of select semivolatile organics on a variety of CNTs, an important step in the expansion of its analytical platform. Another aim is to explore these sorbents on a comparative basis and assess their application in a microtrap.

4.2 Experimental

4.2.1 Materials

An impure MWNT sample covered with NTC and synthesized via CVD using ethanol as a carbon source and Ni as the catalyst [62, 69] was used as a sorbent. This sample is referred to as MWNT-1. To eliminate the NTC, initially these tubes were passed through 106 micron sieve, Endecott Ltd. (London, England) to remove the large particles. The residual NTC from the CNT surface was removed by careful oxidation in the presence of air at 350^{o}C for half an hour. The clean MWNT-1 is referred as MWNT-1C. Purified SWNT and MWNT (referred MWNT-2) were purchased from Cheap Tubes Inc. (Brattleboro, VT, USA). Carbopack^{TM} was purchased from Supelco Inc. (Bellefonte, PA, USA) and was used as a basis for comparison. The CNTs and Carbopack^{TM} were packed inside a 0.5 mm ID capillary to fabricate the microtrap. Each microtrap was packed with 20 mg of sorbent. A vibrator was used to ensure uniform packing. Scanning electron microscopy (SEM) using

Genesis 4000 XMS, EDAX Inc. (Mahwah, NJ, USA) was used to study the morphology of the sorbents. The internal structure of CNTs were examined by transmission electron microscope (TEM) using a Topcon 200 kV ultrahigh- resolution microscope from Topcon Corp. (Tokyo, Japan).

4.2.2 Experimental system

The experimental system is as shown in the Figure 4.1. Trace level (ppm_v) organic standards were generated using a diffusion tube method reported before [64]. These organics flowed with nitrogen through the microtrap continuously while the organics were trapped by the sorbents. The microtrap was resistively heated with a 7-10 ampere pulse of electric current from a power supply, Variac 100/200 Series (Cleveland, OH, USA). Desorption were applied at regular intervals to the microtrap, so that the trapped organics were desorbed and detected by the gas chromatograph. The duration of the pulse was between 0.5 to 2.5 seconds. An electric timer Variac ATC series 365 (Cleveland, OH, USA) was used to control the durations and interval between electrical pulses. A resistor was put in series to control the current through the microtrap. A Gas Chromatograph Varian 3400, Varian Inc. (Palo Alto, CA, USA) 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 Inc. (Folsom, CA, USA) Nitrogen was used as the carrier gas with a flow rate of 10 $mLmin^{-1}$ for the microtraps.

4.3 Results and discussion

4.3.1 Characterization of CNTs

As seen in the SEM image of MWNT-1 in Figure 4.2(a), most of the CNT was covered with NTC. This NTC material consisted of larger particles, whose diameter was in the range of a few microns. The access to CNT sites would be limited in the

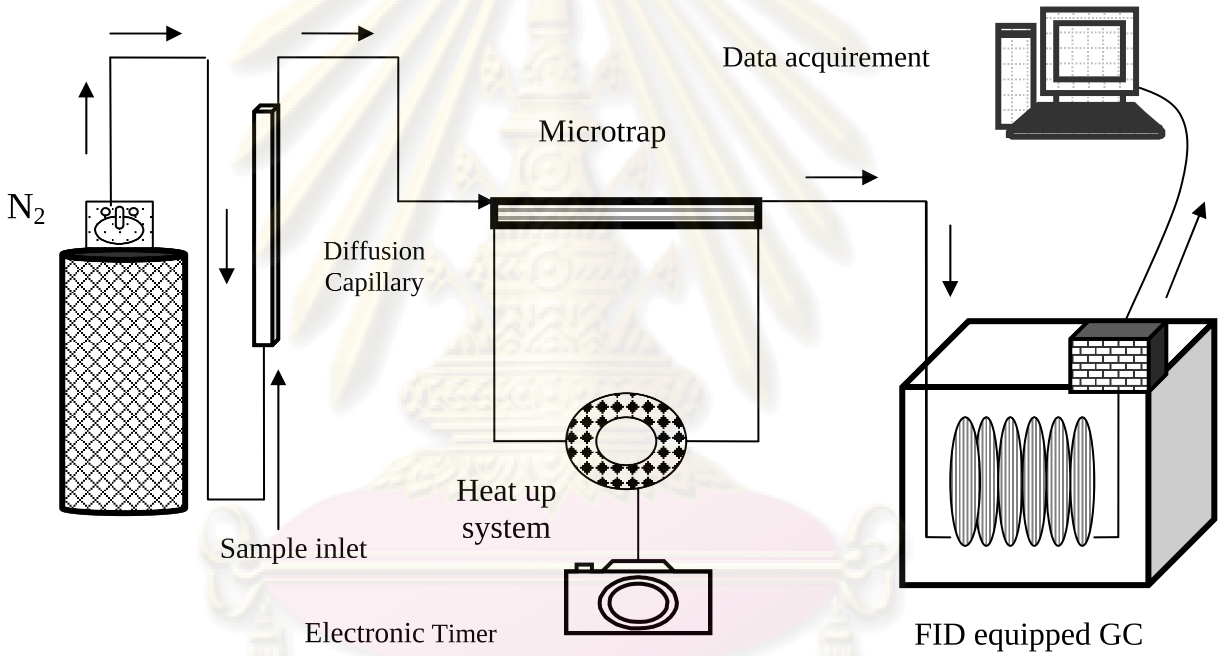
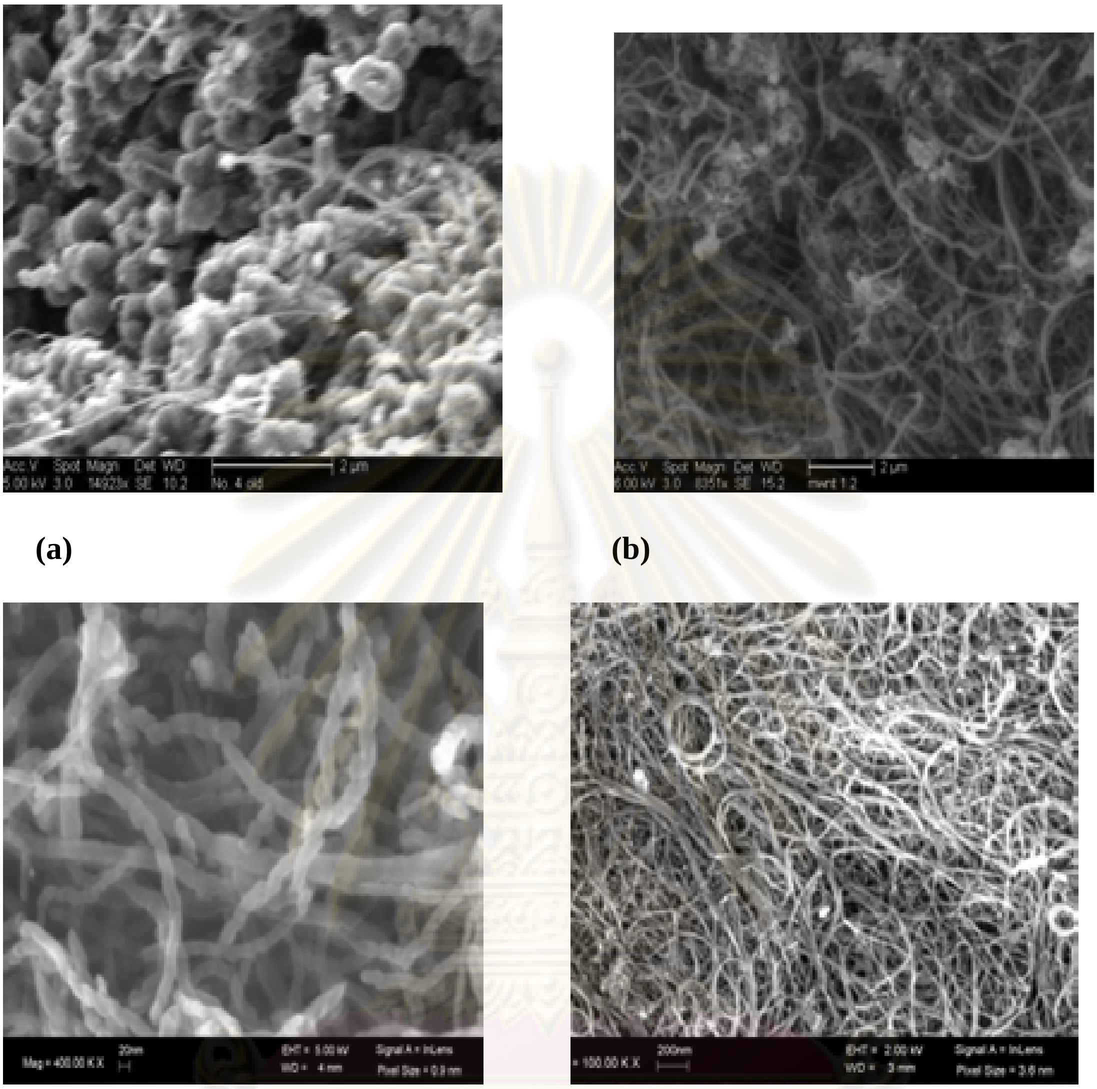


Figure 4.1 **Schematic diagram of the experimental system**.



(a) **(b)**

(c) (d)

Figure 4.2 SEM images of CNTs (a) MWNT-1, (b) MWNT-1C, (c) MWNT-2 and (d) SWNT.

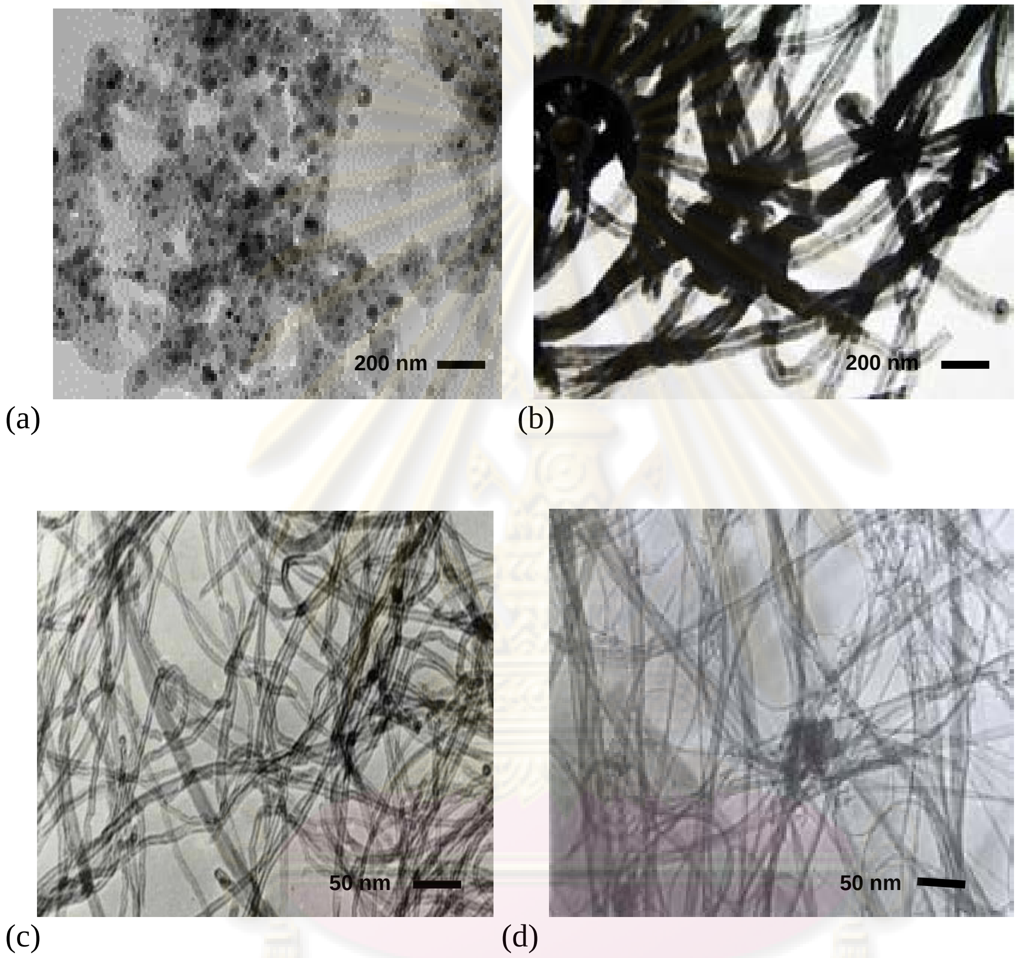


Figure 4.3 TEM images of CNTs (a) MWNT-1, (b) MWNT-1C, (c) MWNT-2 and (d) SWNT.

presence of these. So, several approaches of purification were tested. Figure 4.2(b) is the SEM of MWNT-1C, which was cleaned by sieving to remove the larger particles followed by oxidative annealing in the presence air at 350 ^{o}C. This eliminated much of the NTC on the CNT surface. Longer exposure to oxygen at elevated temperature damaged the nanotubes. Subsequently the annealing was restricted to 30 minutes. As seen in Figure 4.2(b), the CNTs surface was exposed and adsorption on these sites was possible.

Figures 4.2(c,d) present the SEM images of MWNT-2 and SWNT respectively. They had satisfactory levels of purity and no further cleaning was necessary. The images reveal that the lengths of the CNTs ranged from a few hundreds of nanometers to micrometers while the average diameter was between 10-20 nm for SWNT and 20-40 nm for MWNT-2.

TEM image of MWNT-1 in Figure 4.3(a), confirmed that unclean CNTs were covered with NTC, which would have restricted the organic molecules from reaching the CNT surface. After purification, much of the NTC was removed, which are clearly seen in the SEM and the TEM images (Figures 4.2(b), 4.3(b). TEM images of MWNT-2 and SWNT are shown in Figures 4.3(c, d) respectively. Internal structure of MWNT-2 (Figure 4.3(c)) revealed that these were multiwalled while from Figure 4.3(d) it was obvious that these were single walled tubes. These nanotubes were quite clean with little NTC on the surface.

4.3.2 Quantitative desorption from CNTs

If CNTs are to be used for the sampling of SVOCs, high capacity and quantitative desorption will both play important roles. Based on previous studies [55-56], SVOCs are expected to have high breakthrough volumes, and desorbability is the key to their success as sorbents. Quantitative desorption is important for all analytical applications like air sampling. For example, rapid desorption from a microtrap sorbents is essential for producing a sharp concentration pulse to serve as an injection for GC or GC/MS. During resistive heating, rate of desorption depends upon the energy supplied in terms of voltage and duration of the electrical pulse. The energy generated, is computed:

$$\text{Energy} = I^2R\,t \tag{4.1}$$

where I is the current (in amperes), t is the duration of desorption pulse (in seconds) and R is the electric resistance (in ohms). When tube is heated rapidly (several hundred ^{o}C/ second), the resistance of microtrap varies and it is difficult to estimate the total energy. Empirically, the energy supplied is proportional to the duration of the desorption pulse and the applied voltage.

The desorbability of the different sorbents was studied by increasing the duration of the pulse at constant voltage. Figure 4.4, is a plot of response as a function of energy supplied or pulse duration. With SWNT, desorption was initiated with a 0.5 second pulse and it reached its maximum within 1 second. Beyond this the response remained constant i.e., quantitative desorption had been achieved. With MWNT-2, the detector response was initiated with a 0.5 second pulse, and quantitative desorption was achieved with 1.5 seconds. On the other hand, MWNT-1C reached a steady state only after 2.5 seconds. It is clear that desorption from SWNT required the least amount of energy followed by MWNT-2 and MWNT-1C. The SWNT has the highest surface to volume ratio, and is known to have very high thermal conductivity, therefore the easiest to desorb. MWNT-2 was easier to desorb than MWNT-1C probably because the latter still had some residual NTC, adding to the diffusional

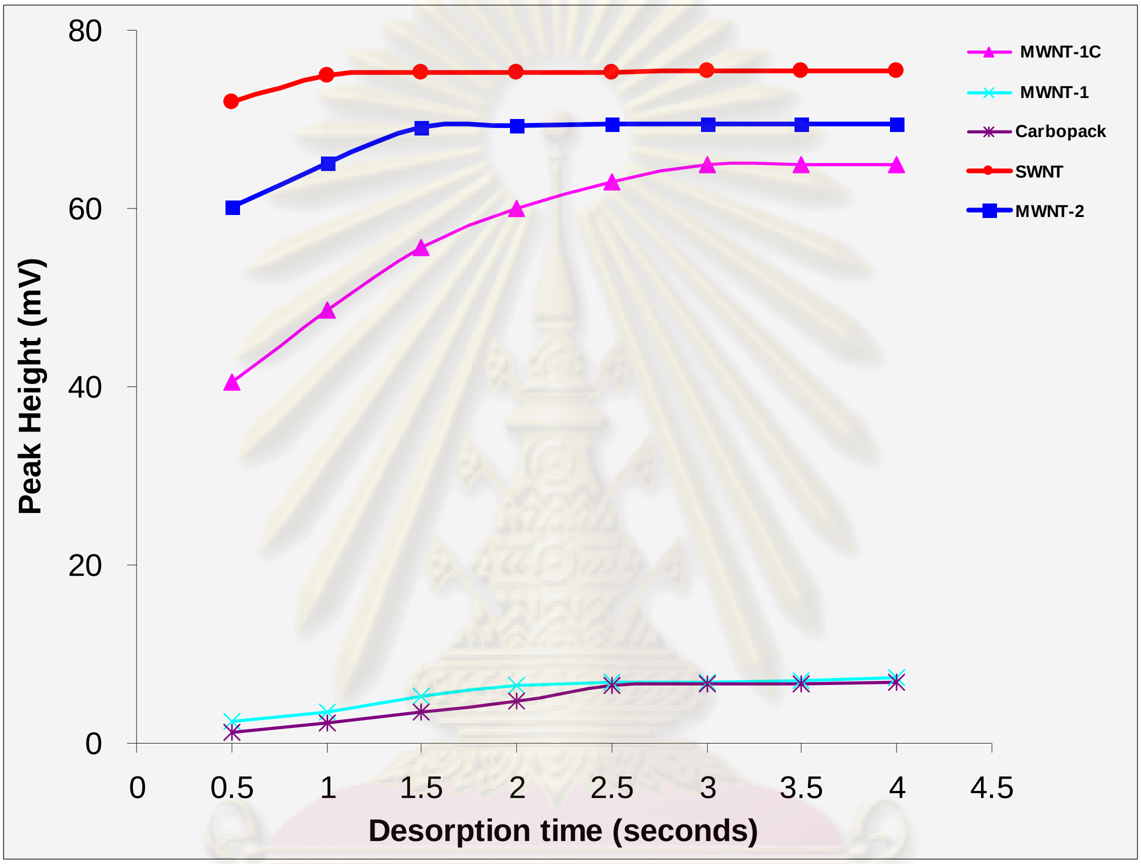


Figure 4.4 Detector response at different pulse durations using ethyl benzene as analyte. The microtrap was heated with 50 volts of power. Injections were made at every 2 min.

resistance to mass transfer. MWNT-1 and Carbopack^{TM} showed relatively poor desorbability and the levels reached at 2.5 seconds may not even be quantitative, although the response appeared to flatten out. The high energy requirement for the desorption of SVOCs from these sorbents is attributed to slower diffusion controlled release from their porous structures. Another important factor is the thermal conductivity or heat flow. The SWNT is known to have high thermal conductivity around 1750 W m^{-1} K^{-1} and the conductivity of MWNT is reported be of the order of 200 W m^{-1} K^{-1} . The thermal conductivity of the Carbopack^{TM} and MWNT-1 are expected to be lower [72].

Figure 4.5(a), represents a series of desorption profiles for ethyl benzene. At least 50 V was necessary for quantitative desorption of ethyl benzene from SWNT for a 2 seconds desorption pulse. Increasing the voltage did not increase the response any further. Under the same conditions, quantitative desorption from Carbopack^{TM} was not possible. The desorption began at 20 V, but there was no evidence of quantitative desorption even at 80 V. Figure 4.5(b), presents response as a function of applied voltage. Both SWNT and MWNT-2 demonstrated quantitative desorption at 50V, but MWNT-1C required 70 V for the same. The trend for MWNT-1 was similar to Carbopack^{TM}. So it is evident that the purification altered the desorption characteristics rather dramatically.

The relative rate of desorption from a sorbent was estimated from the peak width. Narrow desorption band indicated rapid desorption while a broad one the opposite [65]. Figure 4.6(a), shows the desorption profile of naphthalene for SWNT, MWNT-1 and Carbopack^{TM}. The others are not presented here for brevity. It was the

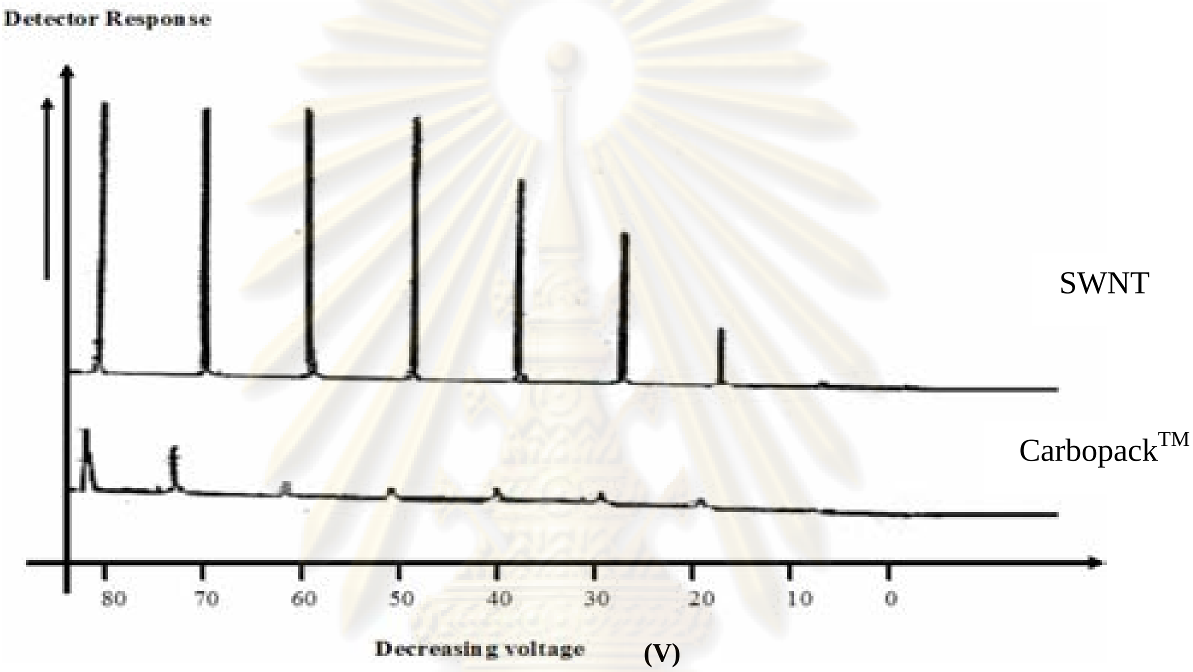


Figure 4.5 (a) Detector response as a function of applied voltage using ethyl benzene as the analyte. The pulse duration was 2 seconds. Injections were made every 2.0 min.

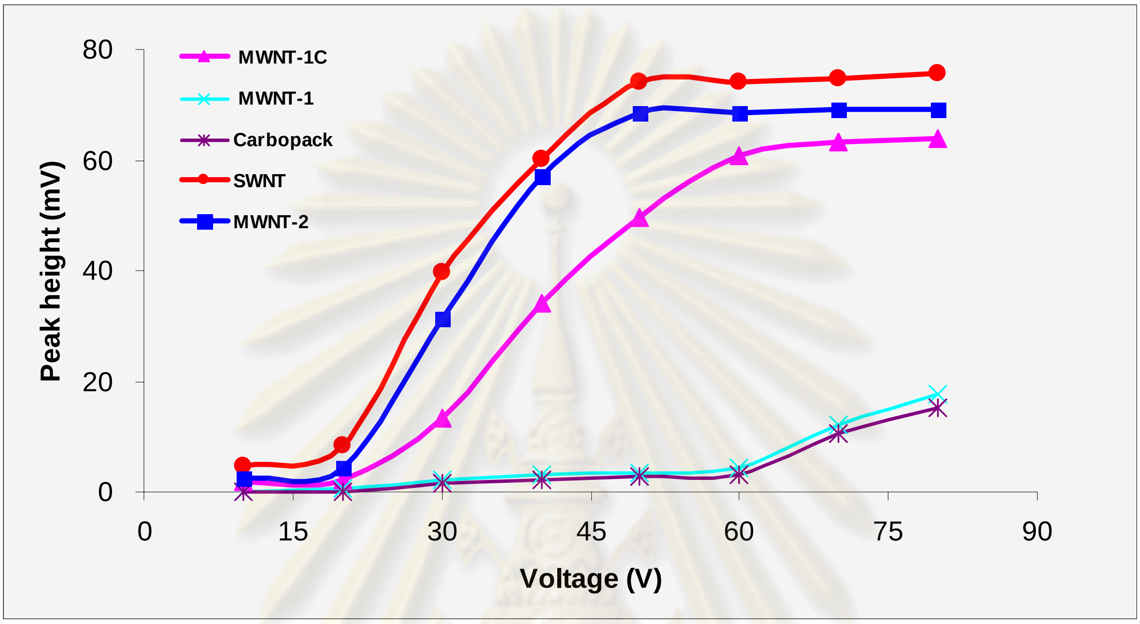


Figure 4.5 (b) Detector response at different voltages for different sorbents using ethyl benzene as the analyte. Pulse duration was 2 seconds and injections were made every 2.0 min.

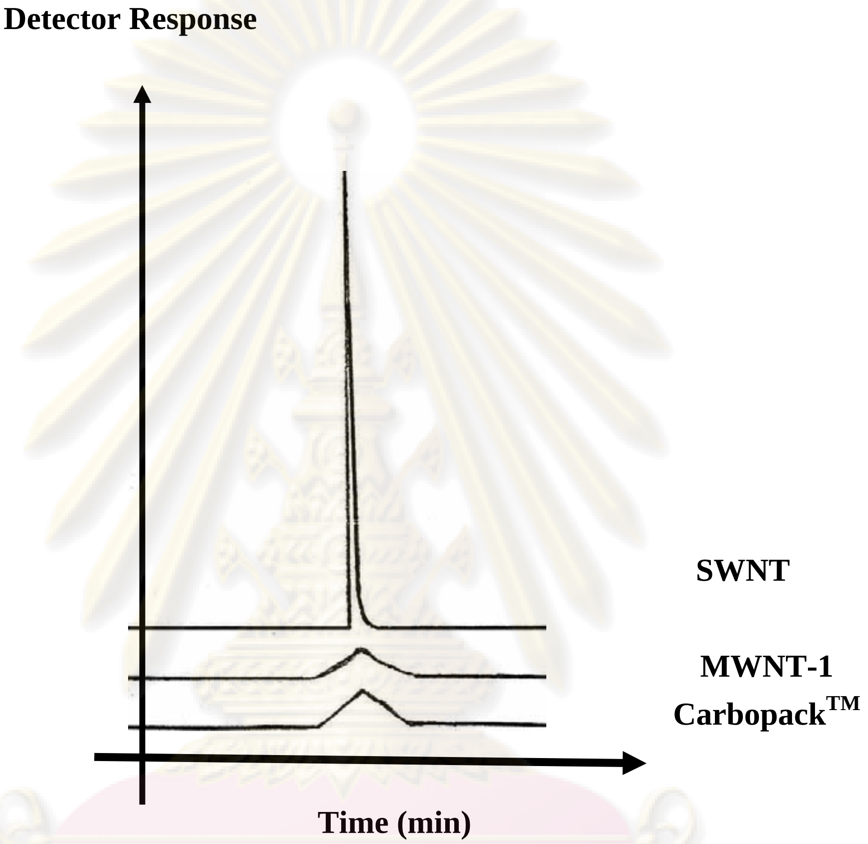


Figure 4.6 (a) Desorption profile of Naphthalene from Packed microtrap with different sorbents: Pulse duration was 2.5 seconds and the applied voltage was 80 V.

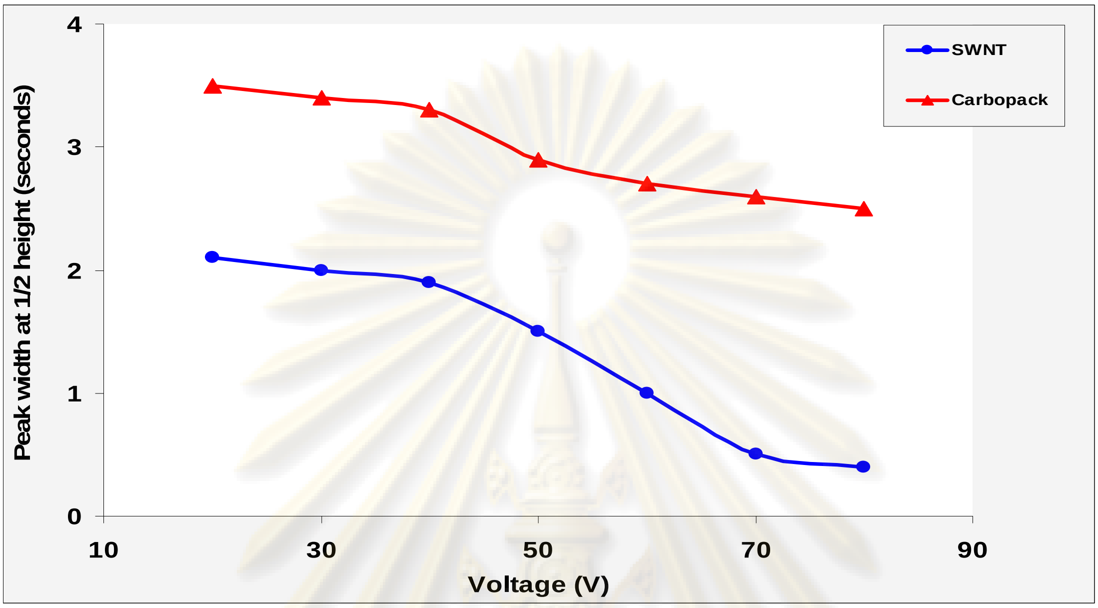


Figure 4.6 (b) Peak width at half height as a function of applied voltage using Phenol as the analyte. The desorption pulse was 1 second and injections were made every 1.0 min.

least volatile of the compounds studied here. Under the same voltage and pulse duration, the desorption band from the SWNT was much narrower than that from either Carbopack^{TM} or MWNT-1. Under the same conditions the peak width at half height for SWNT, MWNT-2 and MWNT-1C were 0.5, 0.56 and 0.65 seconds respectively. The corresponding peak width for CarbopackTM was 4.0 seconds or 800% higher. It is also estimated that desorption of naphthalene from CarbopackTM was not quantitative. The variation in peak width at half height as a function of voltage for SWNT and Carbopack^{TM} is shown in Figure 4.6(b), where phenol was used as the analyte. In case of SWNT, the peak width at half height decreased from 2.1 to 0.4 seconds, while that for Carbopack^{TM} decreased from 3.5 to 2.5 seconds when the voltage was increased from 20 to 80 V. The decrease in the band width for SWNT was much faster than Carbopack^{TM}.

4.3.3 Breakthrough characteristics as a function of sorption capacity

The trapping efficiency of a sorbent depends upon the surface area as well physi / chemisorption on the surface. The sorption capacity is usually estimated by studying the breakthrough time, which was defined as the time required by an analyte to elute through, or the time for which the organics are retained in the CNTs [61]. But breakthrough time decreases with increase in flow rate of the carrier gas. So, there is linear relationship between Breakthrough time and flow rate whereas BTV is calculated from breakthrough time and is a product of breakthrough time and flow rate, so it is directly proportional to the latter. Breakthrough time is known to be a function of the capacity factor, length, and flow rate [67]. The microtrap was operated at various injection intervals to calculate the breakthrough time. Increasing injection interval enhanced the detector response as more organics were accumulated by the

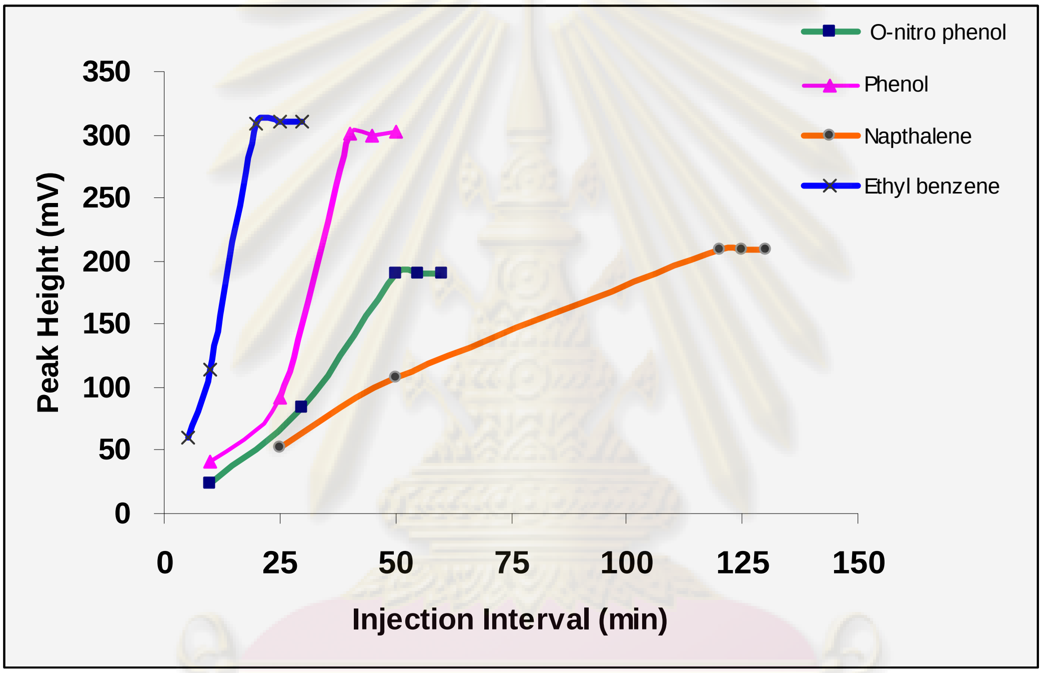


Figure 4.7 Detector response at different injection intervals for SWNT. The desorption pulse is 2.0 seconds while the applied voltage was 60 V.

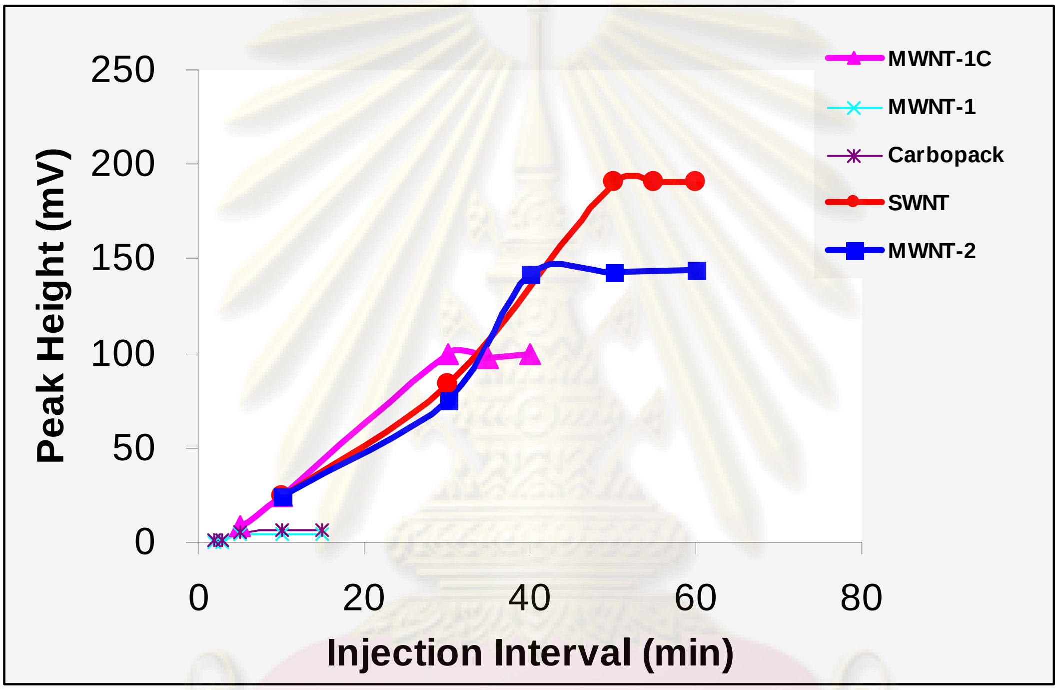


Figure 4.8 Detector response at different injection intervals for o-nitro phenol The desorption pulse was 2.5 seconds while the applied voltage was 80 V.

microtrap. Once the SVOCs began to breakthrough, the response did not increase any further when the injection interval was increased. So the breakthrough time of the microtrap was computed as the time required to reach the maximum response. This technique has been described in previous publications [1,4,55-56].

The four SVOCs with different functional groups represented a wide range of volatility. Typical breakthrough profiles for SWNT are seen in Figure 4.7, with naphthalene showing the longest breakthrough time. The other CNTs showed similar sorption trend, and are not presented here for brevity. SWNT was effective in trapping the polar as well as the non polar organics.

The breakthrough of ortho-nitro phenol on different sorbents is shown in Figure 4.8. All the CNTs showed considerable higher sorption capacity than Carbopack^{TM}, the only non- nanotube in the group. The MWNT-1, was similar to Carbopack^{TM}, as most of the sorption occurred on the NTC, which was morphologically closer to Carbopack^{TM} than the CNTs. The purification to MWNT-1C led to a 600% enhancement in breakthrough time. This demonstrates the importance of impurity elimination when CNTs are utilized for sorption purposes.

Table 4.1 Breakthrough times (min) of different compounds on CNTs and Carbopack^{TM}

No.	Type of sorbent	Ethyl benzene	Phenol	O-nitro phenol	Naphthalene
1	SWNT	20.0	40.0	50.0	120.0
2	MWNT-2	15.0	30.0	40.0	110.0
3	MWNT-1C	5.0	20.0	30.0	90.0
4	MWNT-1	3.0	10.0	5.0	15.0
5	Carbopack^{TM}	3.0	10.0	5.0	12.0

The breakthrough times for different compounds on the CNT sorbents are listed in Table 4.1. The SWNT showed the highest adsorption capacity in terms of breakthrough volume per unit mass. This is attributed to the higher aspect ratio of these nanotubes. For example, the breakthrough time of naphthalene on SWNT was 10 times higher than that on Carbopack^{TM} or MWNT-1. MWNT-1C showed breakthrough time that were closer to MWNT-2, but consistently lower. This was attributed to higher amount of impurities in the former, along with other factors, such as, different size and morphology.

Among all investigated CNTs materials, SWNT was probably the best nano-structured sorbent in terms of rate of desorption and breakthrough time of the SVOCs. Modification operations of sieving and oxidative heating significantly enhanced the desorption rate of CNTs. Owing to higher sorption capacity and fast desorption rate, physisorption may be more promising concept for sorption on the CNTs. These results suggest the potential application of CNTs for the capture of SVOCs. The important features appear to be non porous nature, large aspect ratio, purity and the presence of active sorption sites which act as efficient traps for organic molecules.

4.4 Conclusions

CNTs packed inside a microtrap and interfaced with gas chromatography was used to study the gas phase preconcentration of trace organics. We demonstrate that CNTs are highly efficient for both retention and rapid desorption for relatively semivolatile organic molecules. The former was characterized by large breakthrough volumes, and fast desorption was demonstrated by narrow desorption band widths. The elimination of NTC from the CNT surface is important because they degrade the performance of these sorbents. However, the NTC could be eliminated by controlled oxidative annealing.

CHAPTER V

MICROTRAPPING WITH FUNCTIONALIZED CARBON NANOTUBES

5.1 Introduction

An ideal CNT is a quasi-1D cylindrical aromatic macromolecule and is expected to be fairly chemically inert. Recently, mounting attentions has been focused on the coherent functionalization of the CNTs to formulate functional nanomaterials with novel properties. Some creative methods have been exercised for the functionalization of the CNTs through a covalent or non covalent interaction, that have led to the formation of a variety of novel nanostructures with variable physical and chemical properties [73-74].

Covalent functionalization is based on covalent linkage of functional entities onto the nanotube’s carbon scaffold. It can be performed at the termini of the tubes or at their sidewalls. Direct covalent sidewall functionalization is associated with a change of hybridization from sp^2 to sp^3 and a simultaneous loss of conjugation. Covalent linkages with CNT are normally achieved through chemical techniques such as carboxylation, amidation fluorination and esterification and have been employed in diverse applications such as reinforced polymer composites and drug delivery. Functionalization also offers the unique opportunity of tailor making sorbents for diverse application [75-81].

Typically, hydrophilicity in the sorbents is accomplished via copolymerizing a polar monomer or chemically modifying a hydrophobic structure with appropriate functional groups [78]. However, in case of CNTs, the improvement in the retention of polar analytes on the sorbents may be easily accomplished by simply introducing polar functionality to the CNT scaffold [79]. Therefore, functionalization may be utilized for the enhancement in analytical and separation chemistry. The purpose of this chapter is to study the variation in adsorption properties of MWNT after covalent functionalization with a polar group with the aim of enhancing the breakthrough volume of polar compounds. In the process, we aim to expand the sphere of analytical application of CNTs as novel nano-sorbents.

5.2 Experimental

5.2.1 Materials and instrumentation

The original MWNT were purchased from Cheap Tubes Inc. (Brattleboro, VT, USA). Carbopack^{TM} was purchased from Supelco Inc. (Bellefonte, PA, USA). All other chemicals were purchased from Sigma Aldrich Inc (St. Louis, MO, USA). The functionalization of CNTs was carried out in a Microwave Accelerated Reaction System CEM Mars (Matthews, NC, USA) fitted with internal temperature and pressure controls. The 100 mL reaction chamber was lined with Teflon PFA$^{®}$ with an operating range of 0~200 °C and 0~200 psi. The Fourier Transform Infrared spectroscopy (FTIR) measurements of functionalized were carried out in purified KBr pellets using a PerkinElmer Spectrum One instrument (Downers Grove, IL, USA). The Thermogravimetric analyses (TGA) was performed using a Q500 TGA from TA Instruments (New Castle, DE, USA) to ensure the functionalization on CNTs.. The internal structure and functional groups on the CNTs were examined by Transmission Electron Microscope (TEM) using a Topcon 200 kV ultrahigh- resolution microscope from Topcon Corp (Tokyo, Japan).

5.2.2 Functionalization of MWNT

The functionalization of MWNT was carried out using procedure reported before [82]. First, the residual metals from were removed via microwave induced reaction with saturated Ethylene diamine tetra-acetate (EDTA) in CH_3COOH]. The purification reaction was carried out for 10 min. This purified sample of MWNTwas referred as MWNT-1.Then this purified sample of MWNT was added to the reaction chambers together with 50 mL of the mixture of 1:1 70% nitric acid and 97 % sulfuric acid. With the microwave power was set to 80 % of a total of 1600 watts and the temperature set at 140°C, the reaction was carried out for 10 min. After the reaction, the suspension was diluted into 50 mL deionized (DI) water, and the mixture was filtered through a 10 µm PTFE membrane paper. Then this sample was vacuum dried at room temperature, the sample (referred f-MWNT) in the powder form was characterized by FTIR, TEM and TGA.

5.2.3 Microtrap fabrication and experiment

The CNTs both (MWNT-1, f-MWNT) and Carbopack^{TM} (used as a basis for comparison) were packed inside a 0.5 mm ID capillary to fabricate the microtrap. Each microtrap was packed with 20 mg of sorbent. A vibrator was used to ensure uniform packing. Trace level (ppm_v) organic standards were generated using a diffusion tube method reported before [61,64,69,83]. These organics flowed with nitrogen through the microtrap continuously while the organics were trapped by the sorbents. The microtrap was resistively heated with a 7-10 ampere pulse of electric current from a power supply, Variac 100/200 Series (Cleveland, OH, USA). Desorption were applied at regular intervals to the microtrap, so that the trapped organics were desorbed and detected by the gas chromatograph. The duration of the pulse was between 0.5 to 2.5 seconds. An electric timer Variac ATC series 365 (Cleveland, OH, USA) was used to control the durations and interval between electrical pulses. A resistor was put in series to control the current through the microtrap. A Gas Chromatograph Varian 3400, Varian Inc. (Palo Alto, CA, USA) equipped with conventional flame ionization (FID) was used for analysis using a 0.53

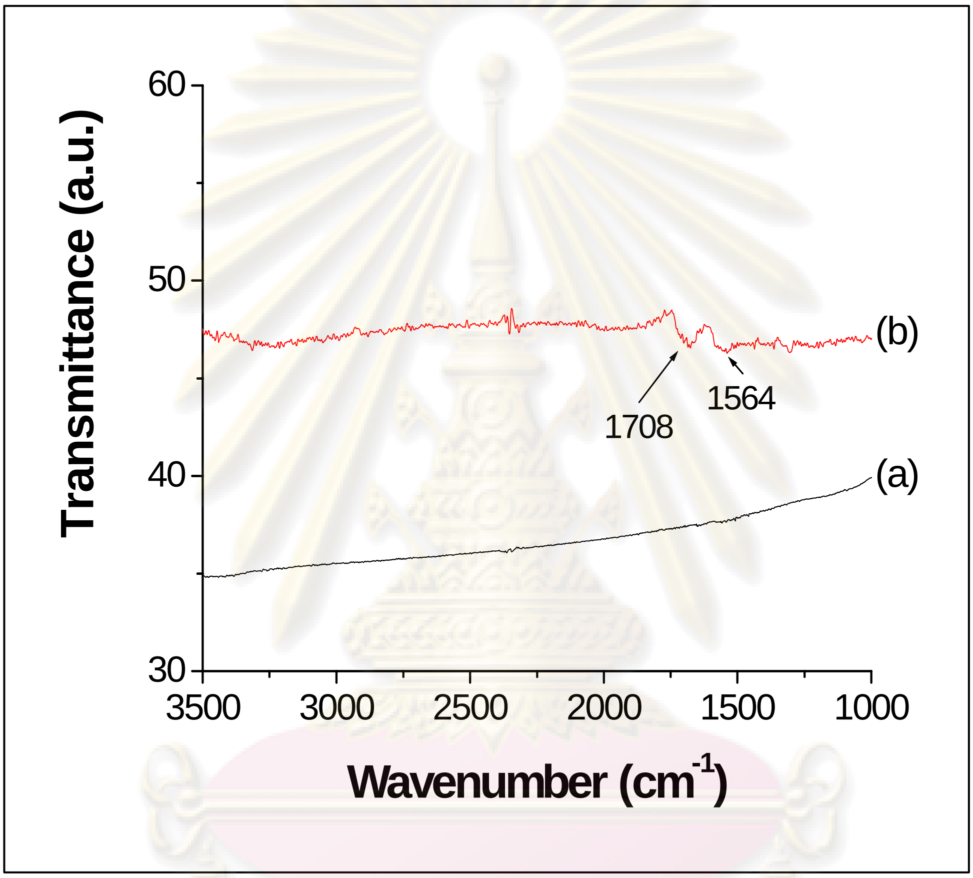


Figure 5.1 **FTIR spectra of; (a) MWNT-1, (b) f-MWNT.**

(a)

(b)

Figure 5.2 TEM images of CNTs; (a) MWNT-1, (b) f-MWNT

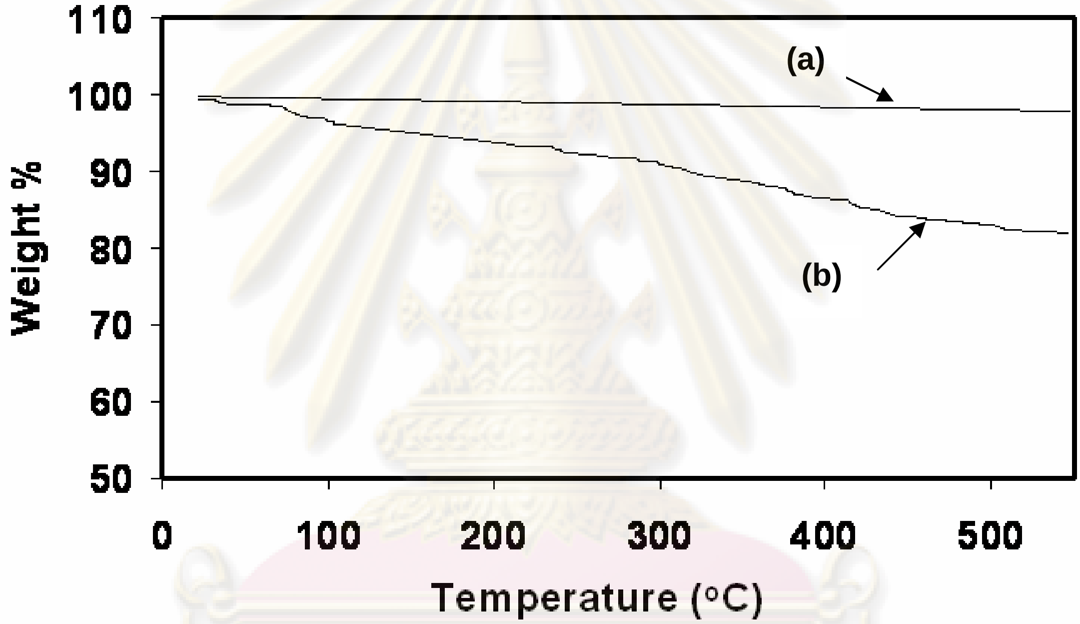


Figure 5.3 Thermogravimetric analysis (TGA) under pure nitrogen at a heating rate of 10 ^{o}C per minute for; (a) MWNT-1, (b) f-MWNT

mm. i.d., 30 m capillary column DB-624, J&W Scientific Inc. (Folsom, CA, USA) Nitrogen was used as the carrier gas with a flow rate of 3 mLmin^{-1} for the microtraps.

5.3 Results and discussion

5.3.1 Characterization of CNTs

The structure of f-MWNT was confirmed by FTIR spectra (Figure 5.1) [84]. The sharp peaks at 1564 cm^{-1} and 1708 cm^{-1} were attributed to the symmetric and asymmetric stretching mode of nitrate groups while these adsorption bands were an indication of –COOH formation.

The TEM image of the MWNT-1 is shown in Figure 5.2(a), and revealed that these were quite clean multiwalled tubes and there were no defects on the sidewalls of the tubes. Figure 5.2(b) presents the TEM image of f-MWNT which verified that, the MWNT-1 after process of amidation, have high degree of functionalization, and were attached to the tubular structure at different places.

TGA was also used to assure the functional groups on the nanotubes, and the results were compared with MWNT-1. The heating was carried out at 10 °Cmin^{-1} from room temperature to 550 °C using a flow of pure nitrogen. The TGA traces (Figure. 5.3) shows that the MWNT-1 showed no weight loss. However, the weight loss for f-MWNT was 19.31 %, which was attributed to the various functional groups.

5.3.2 Breakthrough characteristics of the microtrap

The trapping efficiency of a sorbent depends upon the surface area as well physi / chemisorption on the surface. The sorption capacity is usually estimated by studying the breakthrough time, which was defined as the time required by an analyte to elute through, or the time for which the organics are retained in the CNTs. To calculate the breakthrough time (t_b) of a microtrap several equations have been suggested. The basic principle of these was 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 [20]

$$t_b = \frac{W_c}{C_0 Q}\left[W_s - \frac{\rho Q}{K\gamma}\ln\left(\frac{C_0 - C}{C}\right)\right] \qquad \textbf{(5.1)}$$

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 (mLmin^{-1}), ρ is the density (gmL^{-1}), $K\gamma$ is the sorption rate constant min^{-1}), Co is the inlet concentration (mgmL^{-1}), and C is the breakthrough concentration mgmL^{-1}). Practically, the Breakthrough time 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 organics 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 requires reaching the maximum response [4,56].

Six organic compounds represented a wide range of volatility with varying polarity were analyzed and their properties in terms of boiling point, dielectric constant and density are presented in Table 5.1.

Table 5.1 Properties of the Polar and non-polar organic compounds.

Organic compounds	Chemical Formula	Boiling point (°C)	Dielectric constant	Density (gmL^{-1})
Hexane	CH_3-CH_2-CH_2-CH_2-CH_2-CH_3	69	2.0	0.655
Benzene	C_6H_6	80	2.3	0.879
Toluene	C_6H_5-CH_3	111	2.4	0.867
Dichloromethane (DCM)	CH_2Cl_2	40	9.1	1.326
Propanol	CH_3-CH_2-CH_2-OH	97	20	0.803
Ethanol	CH_3-CH_2-OH	79	24	0.789

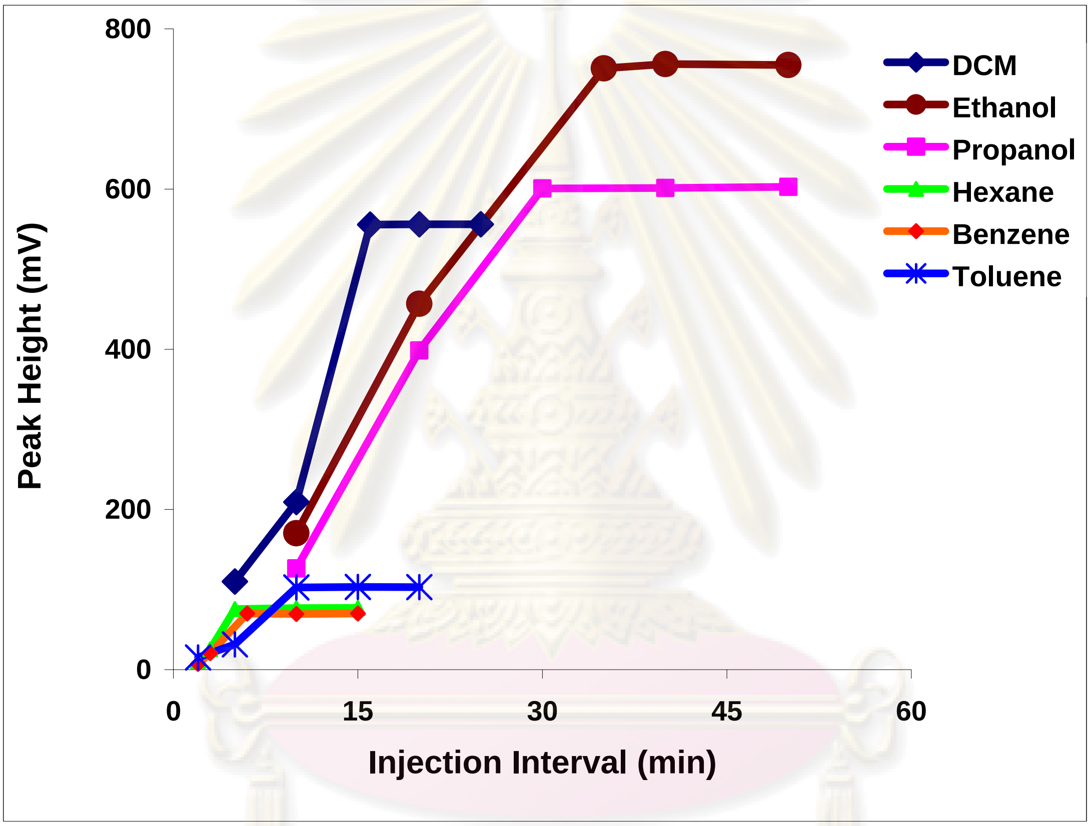


Figure 5.4 **Detector response at different injection intervals for f-MWNT microtrap.**

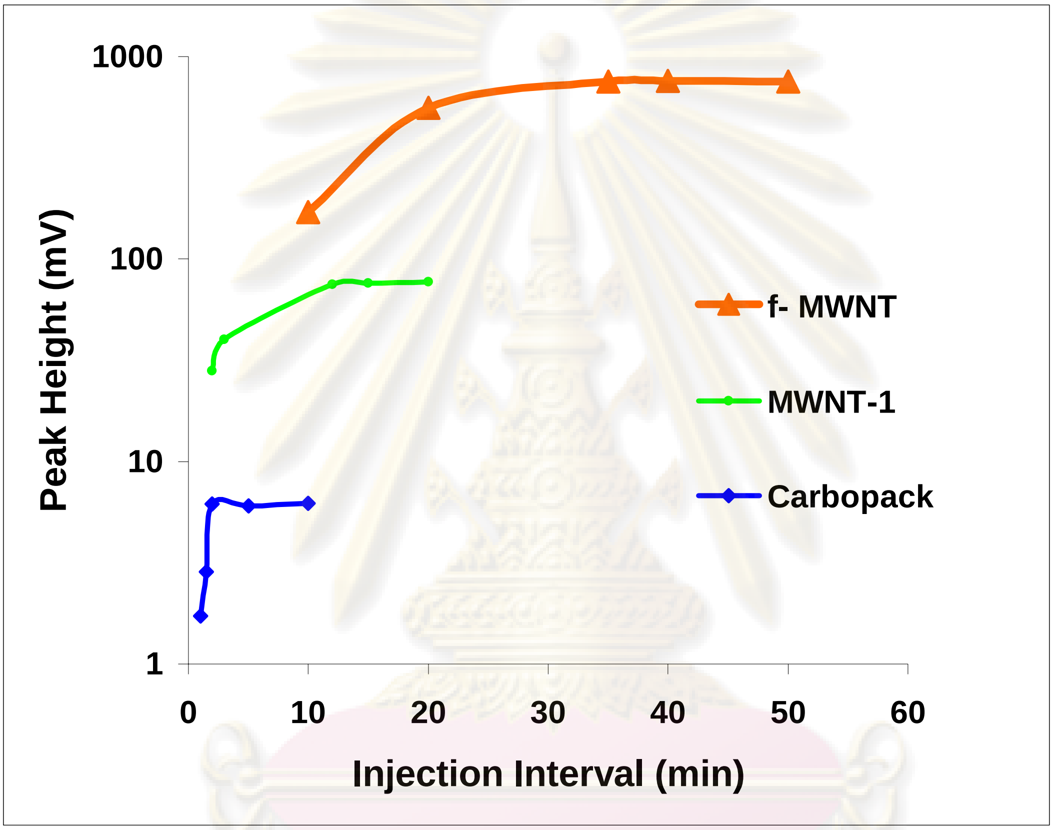


Figure 5.5 **Detector response as a function of injection interval for ethanol using microtraps containing different sorbents.**

Typical breakthrough profiles for f-MWNT at 25°C are seen in Figure 5.4, with ethanol showing the longest breakthrough time and hexane was the lowest. While the comparison of f-MWNT, MWNT-1 and carbopack, when it comes to the retention of ethanol at 25°C is shown in Figure 5.5. For the same mass of sorbent, CNTs showed significantly higher detector response in order of 100 of magnitude as compare to carbopack, the only non tubular carbon sorbent in the group.

The breakthrough time for different organic compounds on the MWNT-1, f-MWNT and carbopack at 25°C are listed in Table 5.2.

Table 5.2 Breakthrough times (min) with f-MWNT, MWNT-1 and carbopack

Type of Microtrap	Polar Organic compound			Non-Polar Organic compound		
	DCM	Ethanol	Propanol	Hexane	Benzene	Toluene
f-MWNT	16	35	30	5	6	10
MWNT-1	8	12	15	20	20	45
Carbopack	2	2	5	5	6	6

Both types of CNTs showed the higher adsorption capacity in terms of breakthrough volume as compare to carbopack. This is attributed to the higher aspect ratio due to the smaller diameter, which led to the higher specific area. The non-polar compounds were expected to have relatively stronger interactions with CNTs, and had higher breakthrough volume [61,69,83] and was also confirmed by the results of MWNT-1. But this was not seen with f-MWNT, because the introduction of functional groups on CNTs may reduce this interaction, and the breakthrough volume of these were decreased nearly four times (Table 5.2). However, for polar compounds breakthrough time was increased almost 300% for ethanol, 200% for DCM and 200% for propanol from MWNT-1 to f-MWNT respectively. As the polarity of functional groups may provide additional interaction for polar compounds and therefore these happen to be increased.

From Tables 5.1 and 5.2 it appears that the breakthrough times obtained with f-MWNT were directly related to the dielectric constant of the organic compounds. For example, the dielectric constant of ethanol was the highest i.e., 24 of the compounds studied, so it displayed maximum breakthrough time whereas hexane being the lowest and thus, appeared to be minimum.

5.3.3 Desorption of the analytes from the f-MWNT

The desorption of the analytes from the microtrap is the reverse process of sorption and is performed by repeatedly heated electrically the microtrap. Quantitative desorption is important for all analytical applications like air sampling. For example, rapid desorption from a microtrap sorbents is essential for producing a sharp concentration pulse to serve as an injection for GC or GC/MS. The quantitative desorption process can be enhanced by rapid heating pulses [19,22].

Figure 5.6, shows typical desorption profile of a polar and non-polar organic compound generated from f-MWNT. The peak width is a measure of the ease of desorption, and is also an important parameter in chromatographic separation. The low desorption band widths with polar analyte (0.51 seconds) than non-polar (1.27 seconds) a reduction of 2.5 times, proved that the polar analyte are relatively easy to desorb and should provide higher desorption efficiency. The desorption reproducibility is another important factor in monitoring devices. The reproducibility was tested for all organic compounds with f-MWNT (Table 5.3). % RSD values obtained for the retention times and peak widths at half heights. For the retention times, the precision was acceptable as it is close to 2%, and these obtained values were found in good agreement with those with other CNTs desorption [70]. In the case of the peak width at half heights, the values were also acceptable and not much difference was found between both cases. Overall, the f-MWNTs not only have high adsorption capacity for polar compounds but also are desorbed easily.

Table 5.3 Desorption reproducibility in term of retention time and peak width at half height for f-MWNT microtrap

Organic analytes	RSD (%) Retention time (min)	RSD (%) Peak width at half height (seconds)
DCM	1.75	1.59
Ethanol	1.95	1.87
Propanol	1.83	1.99
Hexane	2.09	2.25
Benzene	2.13	2.18
Toluene	2.19	2.17

Rate of desorption can be expressed as a function of temperature by the following Arrhenius type relationship [86]:

$$\mathbf{Log\ (rate\ of\ desorption)} = -\frac{\mathbf{Ea}}{\mathbf{RT}} + \mathbf{Constant} \qquad \mathbf{(5.2)}$$

E_a is the activation energy of sorption reactions, R is the gas constant, and T is the absolute temperature. When log (rate of desorption) is plotted versus 1/T, an almost straight line with slope –Ea/R is obtained within temperature range studied as shown in Figure 5.7. The magnitude of activation energy may give an idea about the type of sorption. Possibility of both physical and chemical adsorption may occur. In physical adsorption equilibrium is usually rapidly attained and easily reversible, because the forces involved in physical adsorption are weak. While chemical adsorption is more specific and

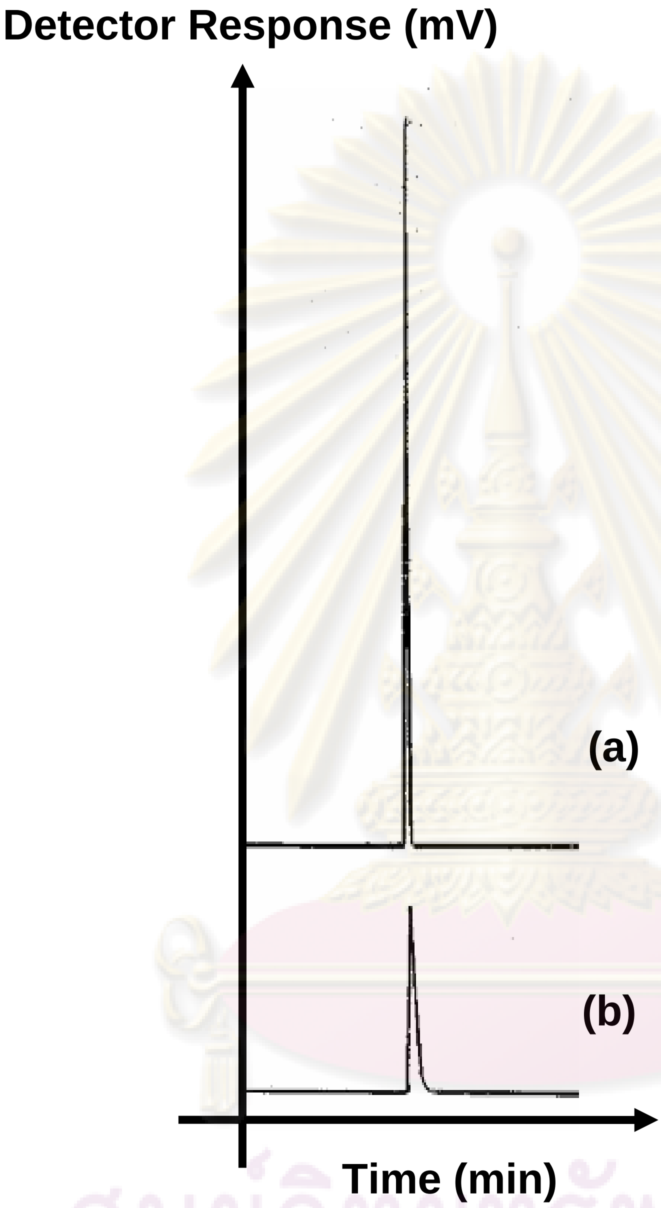


Figure 5.6 **Desorption profile of organic compounds with f-MWNT inside microtrap; (a) polar (b) non-polar**.

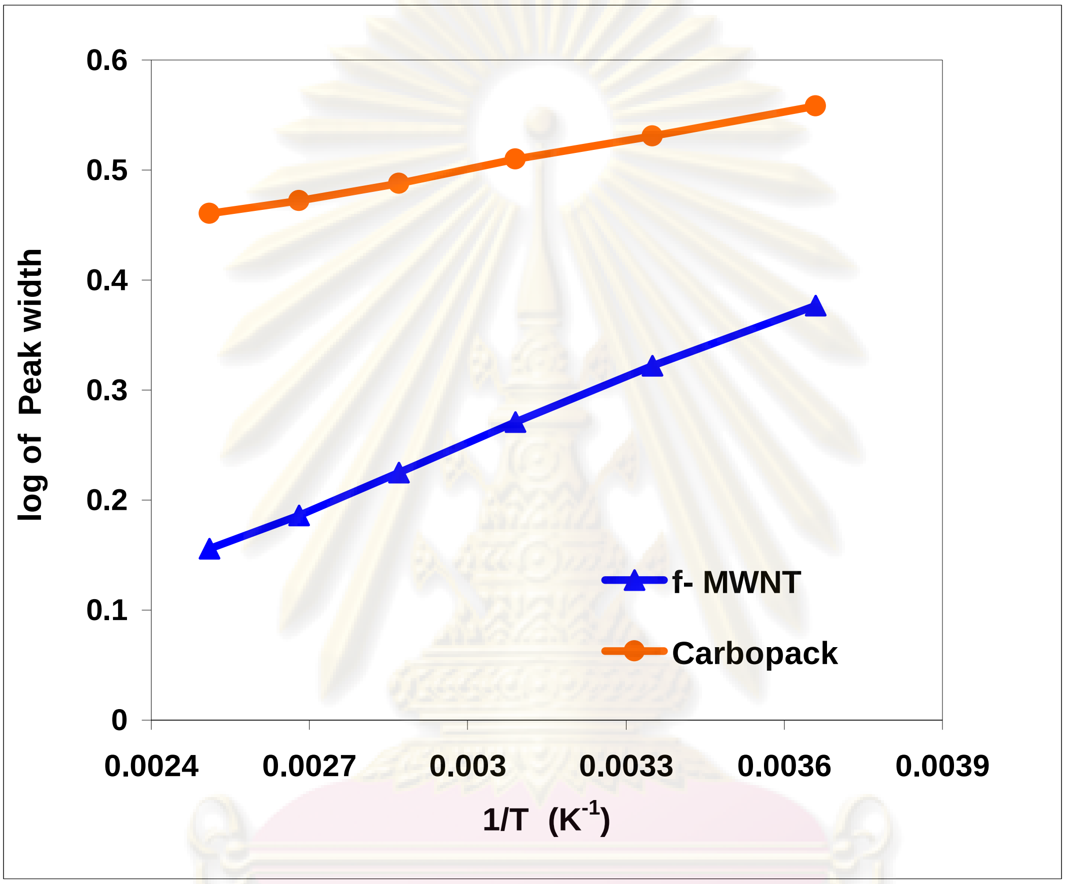


Figure 5.7 **Log of peak width describing the desorption rate from f-MWNT and Carbopack^{TM} as a function of 1/T. Propanol is used as analyte.**

involves forces much stronger, therefore, reversibility is slower and difficult [87]. The values of Ea were found for four times more for Carbopack^{TM} than f-MWNT i.e., – 60 kJmole^{-1} and –240 kJmole^{-1}, suggest that the analyte was more strongly diffused on the porous structure in the former, thus limit the rapid desorption at even higher temperatures. While f-MWNT, rapid desorption with increase of temperature, expresses that sorption on the surface of CNT is more physical in nature.

Commonly, the non-polar organic compounds offer good interaction with perfect CNTs and hence thought to have good sorption capacity for them. But with polar compounds these perfect CNTs surface had very small interactions this should be due to the fact that these are rather chemically inert systems. While, covalent modifications significantly enhanced the adsorption rate of these CNTs and these were proved to be better sorbent for polar analytes.

Conclusions

In summary, we observed that the polar analytes and the functionalized tubes surfaces have more effective interactions. We demonstrate that functionalized CNTs are highly efficient for both retention and rapid desorption for polar organic molecules. The former was characterized by large breakthrough volumes which was raised to 300% than simple CNTs, and fast desorption was demonstrated by narrow desorption band widths that was reduced to 2.5 times. Apart from π–π interaction, polarity had critical role during adsorption, whereas four times reduction in surface activation energy for f-MWNT than carbopack, suggested that interactions were more physical in nature. In conclusion, it can be said the greater anticipations of CNTs as mico-sorbents rely not only on their higher aspect ratio, nonporous nature but also significantly on the fact that how much CNTs are modified specifically to enhance selectivity to particular target analytes.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

This work investigated the possible environmental application of carbon nanotubes (CNTs) as micro-sorbents by integrating them in microtrap with on-line GC system. Carbon nanotubes (CNTs) based microtraps were successfully developed with different formats to monitor the VOCs and SVOCs in gas phase.

6.1 Conclusions

The results obtained from developed microtraps with variety of CNTs for on-line GC system of organics, have shown high-capacity adsorption and fast quantitative desorption, and the process exhibited good reproducibility and long time stability. The important finding this study can be demonstrated by three main subjects. Firstly, CNTs are potential efficient sorbents for on-line microtrap and from high breakthrough volume of organics compounds with CNTs as compare to commercial available sorbent proved that there is a strong interaction between organic molecules and CNTs.

The second is that this study demonstrates importance of the elimination of non tubular carbons (NTC) material from the CNT surface, as they decrease the performance of CNT and a possible method to clean them. Protection of human health and ecosystems requires rapid, precise monitoring devices capable of detecting of organics in air at the trace level. Major improvements in process control, compliance monitoring, and environmental decision-making could be achieved if more accurate, and more sensitive techniques were available. Purification of CNTs offer the possibility of environmental analysis enabled to be more sensitive and accurate.

Thirdly, the functionalization of CNTs offers new option of selectivity and results demonstrated with functionalize CNTs that their selectivity towards the polar organic compounds increased greatly. Environmental management supports the research that addresses new approaches which are more selective in reducing contaminant levels. Specific functional groups on the CNTs surface can impart increased affinity, capacity, and selectivity for pollutants.

6.2 Recommendations and for future work

In general, air samples are more amenable to the application of long-term, time-integrated approaches to sampling and analysis. Application to air samples is more problematic, and the biggest problem area is the preparation required to put such samples into a form amenable to periodic or continuous analysis. Air samples may still require wiping/vacuuming approaches with subsequent labor-intensive extraction and clean-up procedures prior to analysis. Validated methods are needed for such purposes.

The recommendations below were identified during the experience of research. These interesting points may encourage more research to enhancement and improvements in online monitoring system for VOCs and SVOCs in gas phase.

It is recommended that for further developments in the areas of air monitoring it would probably be worthwhile to follow other new developments in online sampling techniques for long-term monitoring, as these appear to avoid the need for laborious recovery of analytes from the samplers or use of solvent extraction or dialysis and the need for expensive cleanup of the extracts before chromatographic analysis.

As this work describes the development of an online sampling consisting of a CNT based microtrap which can be emerging research on microtrap technology, for future in terms of real application potential, it may be worth considering their use for pilot studies. This might be done by preconcentration of a range of analytes which were remained uncovered in this research on CNT based microtrap.

Future studies on adsorption on CNTs under conditions should utilize multiple analytical techniques to fully characterize many components of both the nanotubes and organic used in the study. Additionally, it may possible to modify the experimental instrument used in this study and incorporate more experimental analytical methodologies.

From synthesis part, the purity is essential for CNTs to maximize the available sites and guarantee efficient utilization of their capability. Therefore, a more effective development require in CVD system to have high purity CNTs so that there will be no need to clean them.

The results of this study indicate that there are strong interactions between organic molecules and nanotubes and functionalize CNTs have potential in selective adsorption of organics. Separation is a promising future research topic. One may be able to extend the fundamental surface science of CNTs that may results to study the possible removal of pollutants or even within mixtures, like MTBE from its matrix, like water.

It might also be valuable to follow developments in other sorbents for microtrap technology, so that a widespread comparison can be established for their real world application. As VOCs and SVOCs continue to receive attention as target analytes in diverse range of long-term environmental monitoring studies, as a result, it is anticipated that online microtrap GC system has bright and promising future.

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APPENDICES

APPENDEX A

DIFFERENT CONDITIONS OF CHEMICAL VAPOR DEPOSITION SYSTEM FOR CNTS SYNTHESIS IN LABORATORY

Catalyst Type	Ratio Of Catalyst And Support	Substrate Type	Reaction Atmosphere	Flow Rate Of Inert Gas (mL min^{-1})	Oxidation (min)	Temperature (^{0}C)	Deposition Time (min)
Nickel	1:1	Copper	Argon	100	-	700	60
Nickel and Iron	1:1 +1:1	Copper	Argon	100	30	700	15
Nickel and Iron	1:1 +1:1	Copper	Argon	100	30	700	30
Nickel and Iron	1:1 +1:1	Copper	Argon	100	30	700	60
Nickel and Iron	1:1 +1:1	Copper	Argon	50	30	700	60
Nickel and Iron	1:1 +1:1	Copper	Argons	60	30	700	120
Nickel and Iron	1:1 +1:1	Copper	Argons	60	30	700	300
Nickel and Iron	1:1 +1:1	Copper	Argons	60	30	700	420
Nickel and Iron	1:1 +1:1	Copper	Argons	60	30	700	540

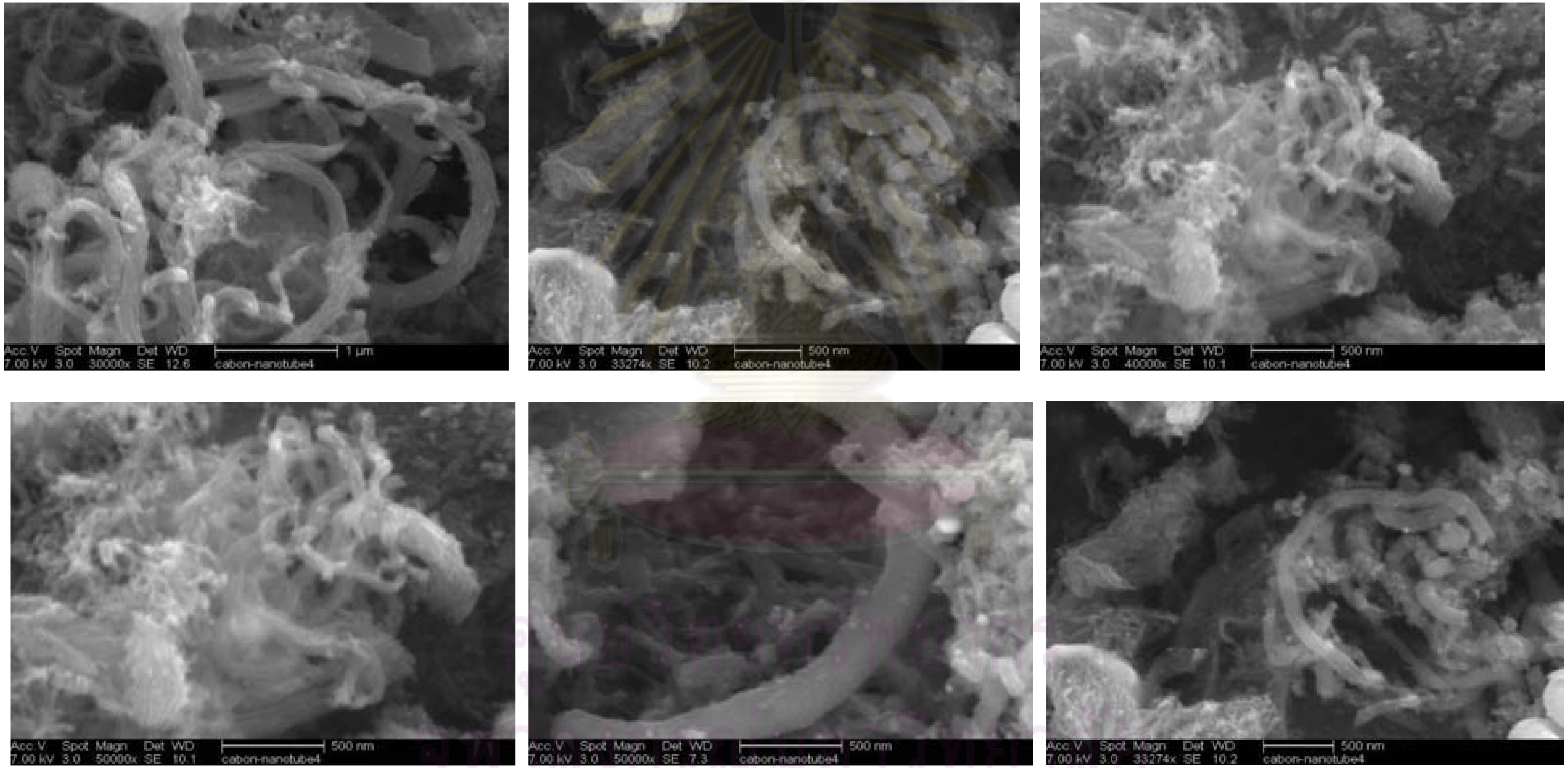
APPENDIX B

COST AND BENEFIT ANALYSIS OF CNTS AND CARBOPACK SORBENTS

Sorbents	**Availability**	**Price in dollar($) per 15 grams**	**Purity (%)**	**Toxicity**	**Performance in % RSD per 10 week usage**	**Operating temperature limit(^{0}C)**	**Compatibility**
SWNT	Commercially (Cheaps tubes)	900	90	So far OK	0.75-1.95	25-400	Both VOCs and SVOCs
MWNT	Commercially (Cheaps tubes)	125	90	So far OK	0.85 -2.01	25-400	Both VOCs and SVOCs
CNTs	Prepared in laboratory by CVD	Very cheap	About 50	So far OK	1.25-2.56	25-400	Both VOCs and SVOCs
Functionlazied-CNT	Prepared in laboratory by CVD	Very cheap	90	So far OK	0.85 -2.01	25-300	Selective for only polar organics
Carbopack^{TM}	Commercially (Supelco)	17.50	100	Irritant if inhaled	2.5-4.95	60-175	Selective for only VOCs

APPENDIX C

SEM IMAGES OF LABORATORY SYNTHESIZED CNTs



APPENDIX D

COMPARISON OF DIFFERENT EPA METHODS WITH ON-LINE GC SYSTEM

Online monitoring system is the fastest way of analyzing samples in analytical science. New frameworks in microtrap sorbent technology suitable for effective analysis will definitely attract further special attention in the forthcoming years.

Method TO-1, analytes are trapped on a porous polymer adsorbent, transferred to a cold trap, and desorbed to the column.

Method TO-2, analytes are trapped on a carbon molecular sieve adsorbent, transferred to a cold trap, and then desorbed to the column.

Method TO-3, analytes are trapped on a cold trap and desorbed to the column.

Method TO-14, a whole air sampler such as a canister is used for sampling. The canisters are then brought back to the lab for analysis.

All these EPA Methods are quite effective in routine environmental analysis and their approximate cost for one sample from 100 US $- US 5000.

On-line system, Code of Federal Regulations (40 CFR 136) requires that air samples stored at 4 °C must be analyzed within 7 days of collection.. Up to 80 % of the error in air analysis is attributed to the delay between sample collection and analysis. Therefore, even if the precision of an on-line method is not as good as that of a lab method, it still provides more accurate results than a conventional lab method because transportation and storage are eliminated.

BIOGRAPHY

Mr. Chaudhery Mustansar Hussain was born on April 30, 1975 in Lahore, Punjab, Pakistan. He received his Bachelor of Science degree in Mathematics and Physics from University of the Punjab, Lahore, Pakistan in 1996. He also did Bachelor of Science in Applied Geology from the same University in 1998. Afterward he started Master of Science in Engineering Geology degree at University of the Punjab, Lahore, Pakistan and graduated in 2000. He worked in govt. and semi-govt. organizations as research consultant for four years. In 2004, he started his Master of Science in Environmental Management at Chulalongkorn University, Bangkok, Thailand and in 2005 he transferred to Doctor of Philosophy in Environmental Management. He completed his Ph.D degree in December 2008. He performed his Ph.D research work at Rajamangala University of Technology, Thanyaburi, Thailand and some part at New Jersey Institute of Technology, Newark, New Jersey, USA. Moreover, his whole education at both graduation and post graduation level was awarded by merit scholarships and teaching assistantships**.**

Presentation and Publications:

1. Chaudhery Mustansar Hussain, Chutarat Saridara, Somenath Mitra, Microtrapping Characteristics of Single and Multi-Walled Carbon Nanotubes, **Journal of Chromatography A,** Volume. 1085, pp. 161-166, 2008.

2. Chaudhery Mustansar Hussain, Chutarat Saridara, Somenath Mitra, Online-Monitoring of Volatile Organic Compounds with Carbon Nanotubes, **First International Thammasat University Conference**, March 2008.

3. Chaudhery Mustansar Hussain, Chutarat Saridara, Somenath Mitra**,** Carbon Nanotubes as Sorbents for the Gas Phase Preconcentration of Semivolatile Organics in a Microtrap, **The Analyst**, Volume 133, pp. 1076-1082, 2008.

4. Chaudhery Mustansar Hussain, Chutarat Saridara, Somenath Mitra, Microtrapping of Volatile Organic Compounds with Carbon Nanotubes, **Nanotech Thailand Conference**, August 2008.

5. Chaudhery Mustansar Hussain, Chutarat Saridara, Somenath Mitra, Microtrapping of Volatile Organic Compounds with Carbon Nanotubes, **Songklanakarin Journal of Science and Technology (**Accepted).

6. Chaudhery Mustansar Hussain, Chutarat Saridara, Somenath Mitra, Microtrapping of Volatile Organic Compounds with Functionalized Carbon Nanotubes, **Submitted.**