CHAPTER 4

NOVEL APPROACH TO MICROTRAP FABRICATION

4.1 Introduction

Carbon filaments with diameters of less than 10 nm were first prepared in the 1970s. However, systematic studies of this material did not begin until the observation of multiwall carbon nanotubes (MWNTs) in the early 1990's [49]. Since that time, carbon nanotubes (CNTs) have been the subject of intense research because of their novel physical and chemical properties. Based on current practices, techniques for CNT synthesis may be classified under three major categories, namely, laser ablation [50], catalytic arc discharge [51] and chemical vapor deposition [52]. However, serious challenges still remain with the large-scale production of CNTs and their implementation in real-world devices.

As CNTs find applications in microelectronics and chemical industries, there arises the need for incorporating them into real world structures and devices. While, laser ablation and arc discharge are excellent techniques for the large-scale production of pure CNTs, they are not suitable for the self-assembly of nanotubes on devices and structures. CVD appears to be the most convenient method for the controlled self-assembly of CNTs on various substrates and devices. Several variations of this technique have been reported in the literature. High purity SWNTs have been grown by the catalytic decomposition of methane [53], by the catalytic disproportionation of carbon monoxide (CO) under high pressures (the so-called high pressure carbon monoxide (HIPCO) process) [54], as well as at atmospheric pressures [55]. Cheng et. al. [56] produced CNTs at 1200°C in a heated flow of benzene together with ferrocene and thiophene precursors to form floating catalytic particles, whereas Maruyama et. al. [57] generated CNTs at temperatures down to 550°C using ethanol under low pressure conditions. Low-pressure CVD using ethylene and propylene was employed by Sharma and Iqbal [58] to observe in real-time the in-situ growth of SWNTs and MWNTs in an environmental transmission electron microscope.

CNTs are expected to play important roles in future gas storage and separations technologies because they represent a novel class of material with varied functionality to facilitate adsorption. The internal pores of the CNTs are small enough to allow small molecules to penetrate. Large sorption surfaces are also available on the outside, and in the interstitial spaces within the nanotube bundles that are held together by van der Waals forces. Larger molecules more easily access these surfaces. The possibility of chemical functionalization of the CNT sidewalls also opens additional possibilities for sorption of different molecules.

CNTs have received much attention as a means of hydrogen (H_2) storage. Adsorption of oxygen, xenon and helium has also been studied quite extensively, both theoretically and by temperature programmed desorption techniques [59]. H_2 storage has been mainly attributed to physisorption both inside the tube and in the interstitial region between tubes in a bundle. The adsorption of organics on CNTs was also studied [60], and is important for applications in separations technology, such as membranes and sorbents used in pollution control. A recent paper reported the adsorption of acetone on CNTs [61]. Chemisorption was suggested based on the high activation energies of desorption, which were significantly higher than those from graphite (known to show physisorption) and the latent heat of vaporization of liquid acetone. Moreover, the activation energies of desorption were comparable to those of covalent bond energies.

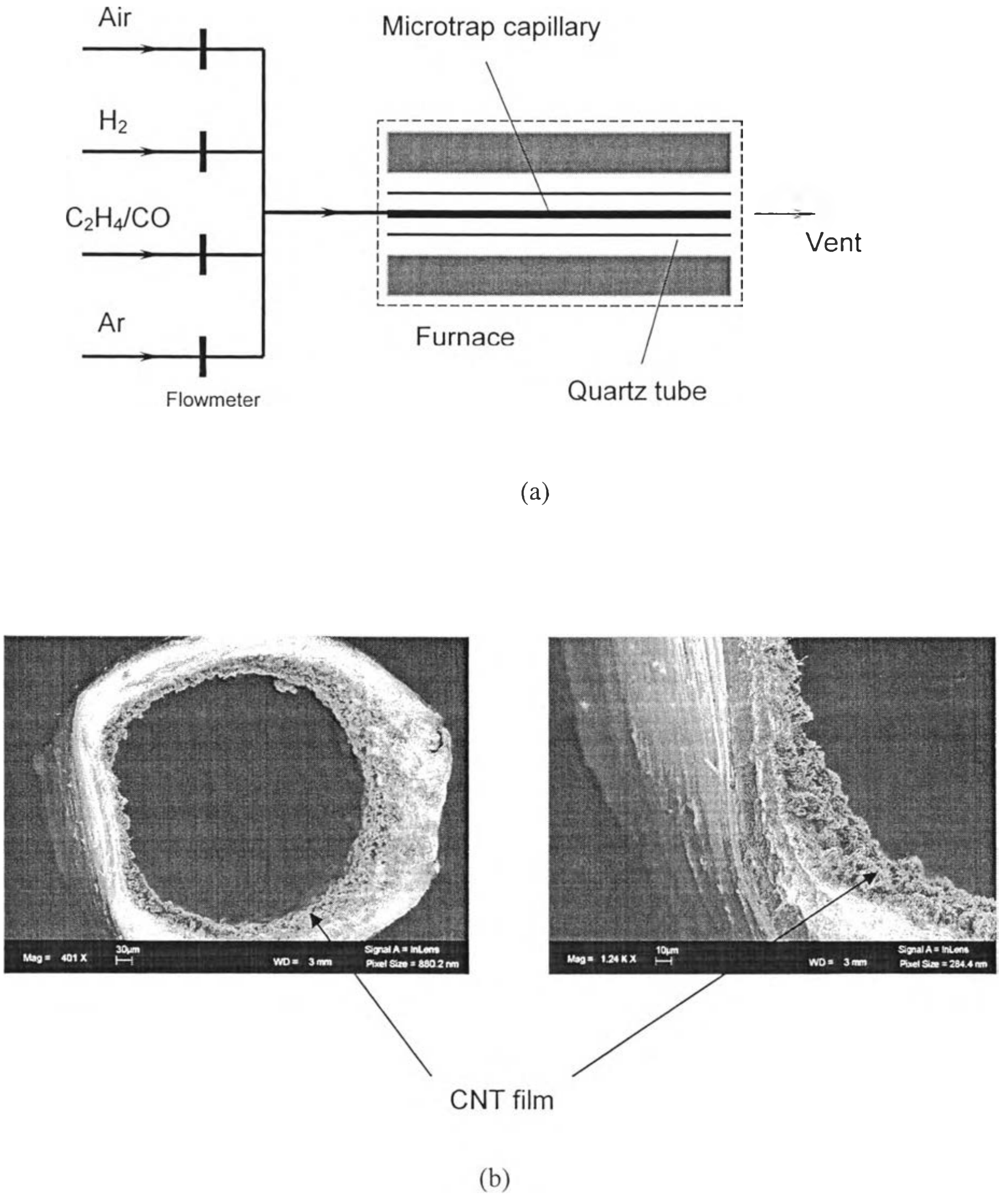
There are two aspects of CNTs that are important for applications in gas storage and separation. The first is the adsorption and the latter is desorption. The physical/chemical affinity between the sorbate and the sorbent need to be optimum for this to occur. One of the issues in H_2 storage in SWNTs is that the desorption during the so-called delivery process is slow [62]. While SWNTs are known to have better mechanical and electrical properties than their multiple wall counterparts, in chemical separations SWNTs and MWNTs are expected to play complementary roles. They are expected to have different affinity and selectivity for compounds with varied functionalities and volatility. It is therefore conceivable that CNTs will emerge as high performance, high temperature sorbents in applications that range from industrial scale gas separations to micro/nano-scale sensors and analytical instruments.

Here the first application of self-assembled CNTs in the nanoscale adsorption/desorption of small organic molecules was investigated. The selected application device is a microtrap that can be used in sensing, and analytical-scale separation, such as gas chromatography (GC). The CNTs are self-assembled as a thin-film on the inside walls of the steel capillary. Trace (parts per million, ppm) levels of organics are then allowed to be adsorbed and concentrated on the CNTs, and then desorbed for detection.

4.2 Experimental

4.2.1 CVD system and conditions.

The self-assembly of CNTs in 500 μm ID capillaries was carried out in a tube furnace by the CVD method described previously [58] and modified for direct growth inside the steel capillaries. This is shown in Figure 4.1. Both CO and C_2H_4 were used as the carbon source for the CNTs. Two types of micro-capillaries were tried here, one was silica-lined stainless steel and the other was untreated stainless steel. Nanocrystals of iron, cobalt and molybdenum are known to catalyze the growth of CNTs [63], so the



(a)

(b)

Figure 4.1 a) Schematic diagram of the CVD set up. b) Crossections of CNT-microtrap grown in steel capillary by CO-CVD.

nanostructured regions of the polycrystalline iron tube provides the catalytic surface for CVD growth and assembly of the nanotubes once the catalyst was deposited. In the case of silica-coated steel, sparse growth appeared, because fine scale porosity in the silica coating probably provided exposed iron for catalytic growth of CNTs. Surface preparation in steel tubing was carried out via a series of oxidation – reduction, which led to the formation of nano-scale structures [64] Catalyst could be deposited by electro depositions of cobalt and molybdenum. These catalysts were used to make the microtrap. This step was carried out in co-operation with another research group within the university. After this, CVD was carried out in a flow of CO or C_2H_4. This process formed the microtrap with a thin-film of CNTs [64].

Previous adsorption studies with organics have been carried out by mixing a gas or a liquid solute with the CNTs and then desorbing the solutes [65]. Trapping of low concentration organics from the gas phase is quite different than from liquid phase [66]. In this study, the adsorption took place from a gaseous stream containing trace levels of organics. The ppm level organic stream containing toluene and hexane was generated by diffusing a controlled amount of the analytes from the diffusion capillary into a flow of N_2. This technique is well known and has been described elsewhere [67]. The stream flowed constantly through the microtrap and the organics were trapped in the self-assembled CNT film. An electrical pulse was applied to the metal capillary at predetermined intervals (every few minutes) to desorb the trapped organics. Duration of the pulse was between 1 to 1.5 seconds, which raised the microtrap temperature to 300-400°C [68]. Rapid heating caused the vapors from the "desorption pulse" to be injected into the detector. A microprocessor-based controller was used to control the interval and duration of the electrical pulses. This technique has been described in details elsewhere [69].

4.2.2 Analytical system.

In general, the microtrap can be used with any sensor or detector. Here it was tested with a conventional flame ionization detector (FID). The analytical system used is shown in Figure 4.2. A Gas Chromatograph (Hewlett Packard 5890) equipped with an FID was used for analysis. A 0.53 mm ID, 30 m capillary column (DB-624, J&W Scientific) was used. Gases such as air, nitrogen, and hydrogen were purchased from Matheson Co., New Jersey. Nitrogen was used as a carrier gas with the flow rate 7 ml/min.

4.3 Results and Discussion

Typical structures of CNTs in the films inside the capillaries are shown in Figures 4.3 a and b. CNTs from CO were relatively short and the diameters ranged from 13 to 100 nm, whereas much longer tubes with the diameters ranging from 25 to 70 nm were formed using C_2H_4. The CNTs deposited were radially aligned inside the tube. Noodle-like structures criss-crossing in different directions and a large number of twisted tubes were also formed. Previous studies have reported the similar formation of nanotubes that were aligned either perpendicular or horizontal to the substrate, particularly under plasma conditions [57]. The thickness of the CNT films grown in the micro capillary could be increased by increasing the CVD deposition time. Films as thick as 30 μm were formed. The thickness is an important parameter as it determines the sorption capacity and mass transfer in the CNT film. Raman spectra taken from the inside surface of the cut capillary did not show the characteristic peaks associated with the strongly diameter dependent radial breathing mode of SWNTs below 300 cm^{-1}, which suggested that SWNTs were not formed under the used conditions.

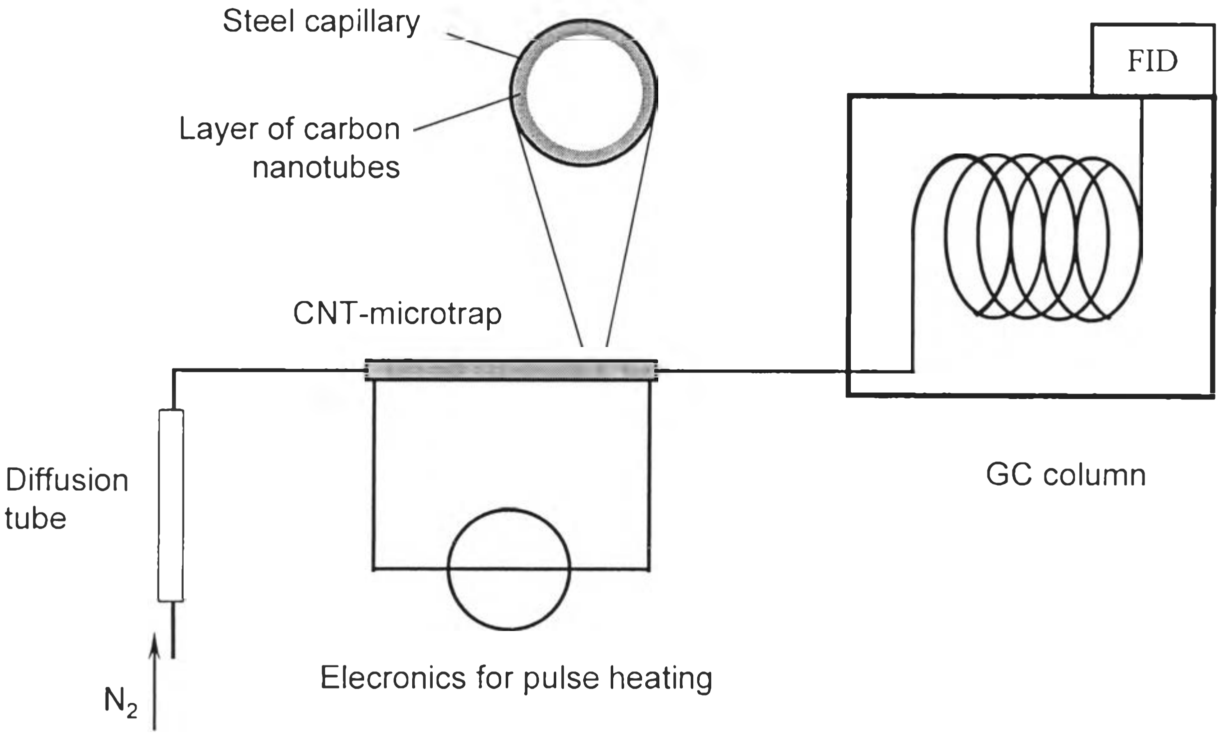
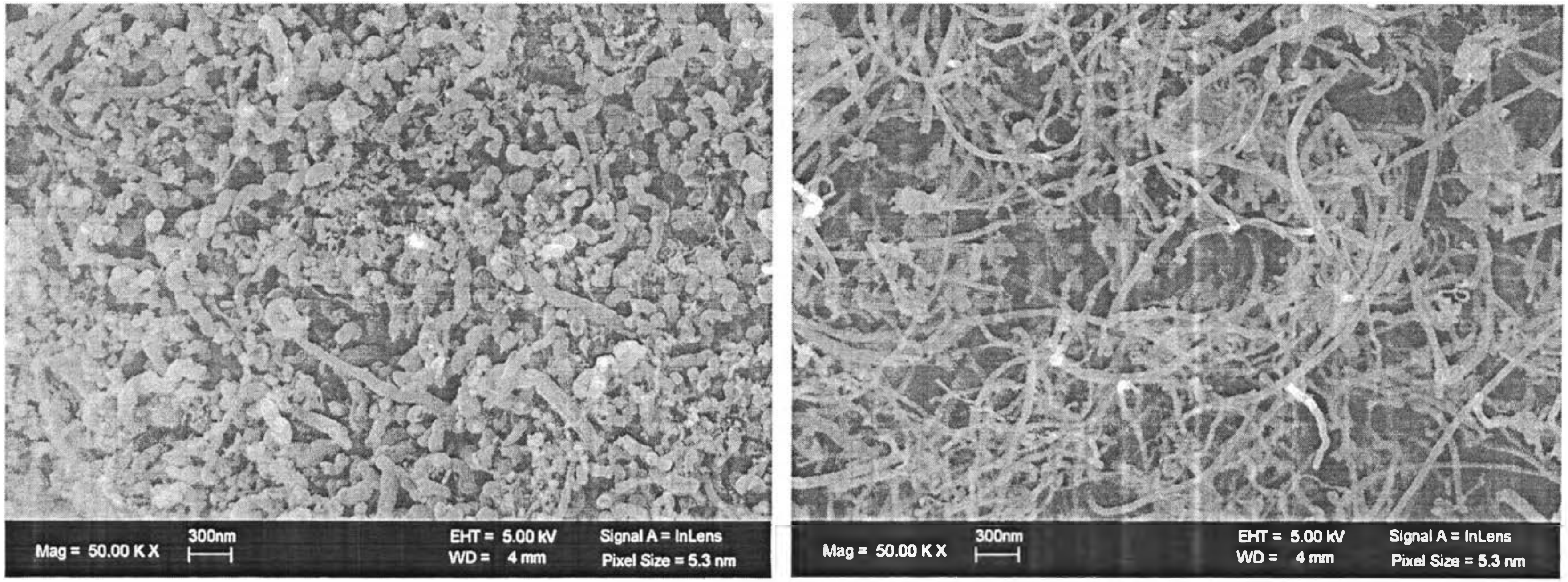


Figure 4.2. Schematic diagram of the experimental set up.



a) b)

Figure 4.3. CNT structure in the microtrap a) by one hour C_2H_4-CVD; b) by one hour CO- CVD.

The gas sample stream containing organics passed the microtrap placed on-line and then was directed to the detector. The organics were alternately adsorbed and then desorbed from the CNT film by electrical heating. The electrical pulses (injections) were made at fixed intervals of time, and a corresponding sequences of signal pulses were observed at the detector. This is shown in Figure 4.4 a. Reproducibility was excellent, and injection pulses could be continued. The coefficient of variation of detector signal was 1.02%. This demonstrated that both the adsorption and desorption from the CNT film was reproducible over long periods of time.

As mentioned before, the two desirable features for sorbate trapping in sensing and separations applications are the strong sorption and fast desorption. These often tend to be mutually exclusive, because conditions of strong sorption do not lead to fast desorption. Thus, both adsorption and desorption processes are important in the CNT-microtrap operation. Fast desorption leads to narrow injection bands. The peak width at half height was around 1.4 sec., which is compatible with high resolution GC, and proved that the desorption from the CNT film was rapid. This was possible in spite of the strong chemisorption of organics suggested previously [64]. Sensing applications require the elimination of any residual or memory effects, here the desorption was found to be completely reversible. The rate of desorption depends on the maximum temperature reached and the heating rate. Because the heat must be transferred from the tube wall through the CNT film, the heat transfer is also an issue. The heating-cooling cycle is known to be of the order of 2-4 seconds. Based on previous studies [15], typical microtrap temperature is between 350 to 400°C, which suggests that the same conditions were appropriate for adsorption-desorption from the CNT film.

The fast desorption from the CNT film allowed the microtrap to be used as an injector for gas chromatography. Figure 4.4 b shows a chromatogram generated by

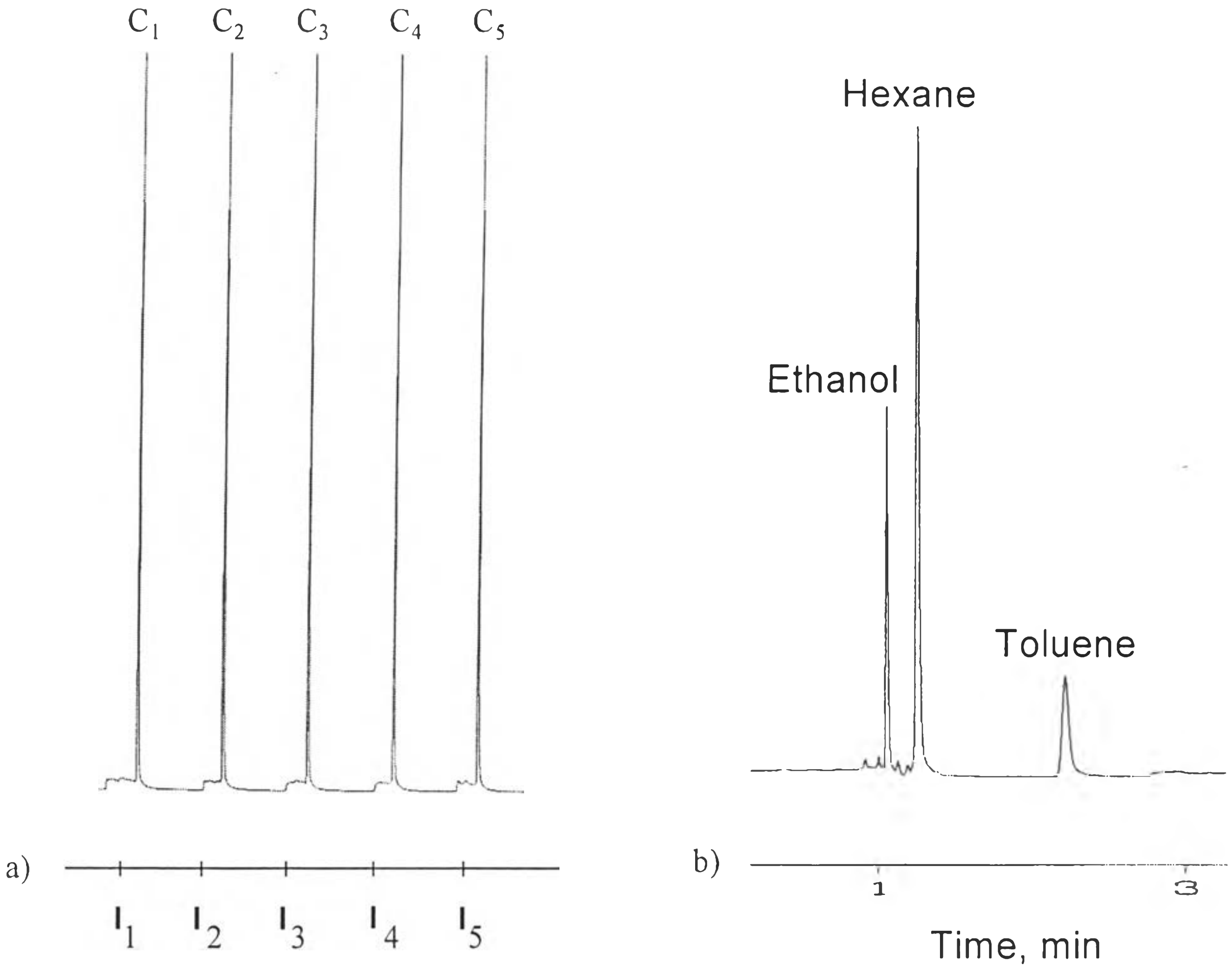


Figure 4.4. a) Sequence of desorption peaks generated using the CNT-microtrap with ppm level toluene as the sample. Injections were made at I$_1$, I$_2$,... (every 2 minutes) resulting in a sequence of concentration pulses C$_1$, C$_2$,... ; b) typical chromatogram generated using the CNT-microtrap as an injector for GC separation.

alternate trapping and desorption of several small molecule organics. The high resolution separation is also attributed to the fast desorption from the CNT film.

The sorption capacity of the CNT film in the microtrap was studied by operating the microtrap at varied injection intervals. As the interval increased, the amount of organics accumulated increased. However, this could not continue indefinitely, as the sample began to break through, and the response could not be increased any further. Figure 4.5 shows the breakthrough of hexane and toluene on the microtrap. The response profile showed a linear increase with the injection interval up to some point after which the response became constant. This is the breakthrough point for the microtrap, i.e., the time for which the organic molecules are retained [23] in the CNT film. Under similar process conditions, such as flow rate, pressure and deposition time, CO formed a lower capacity film compared to that from C_2H_4, which is probably because of higher densities of CNTs formed from C_2H_4 as a precursor. This resulted in different breakthrough time on the microtrap, which were 4.5 and 12 times larger for hexane and toluene, on the microtrap made with the C_2H_4-CVD. The interesting also is the high retention of toluene as compared to the aliphatic hydrocarbon. While a larger retention is expected based on lower volatility of toluene, the unusually large difference (4.5 min versus 35 min) is attributed to the strong π-π interactions between the aromatic toluene and the graphitic ring structure of the CNTs. In general, the trapping capacity of a 2 μm film of CNT was found to be higher than that of a packed bed of commercial activated carbon (Carbotrap®, Supelco Inc., Supelco Park, PA) [23].

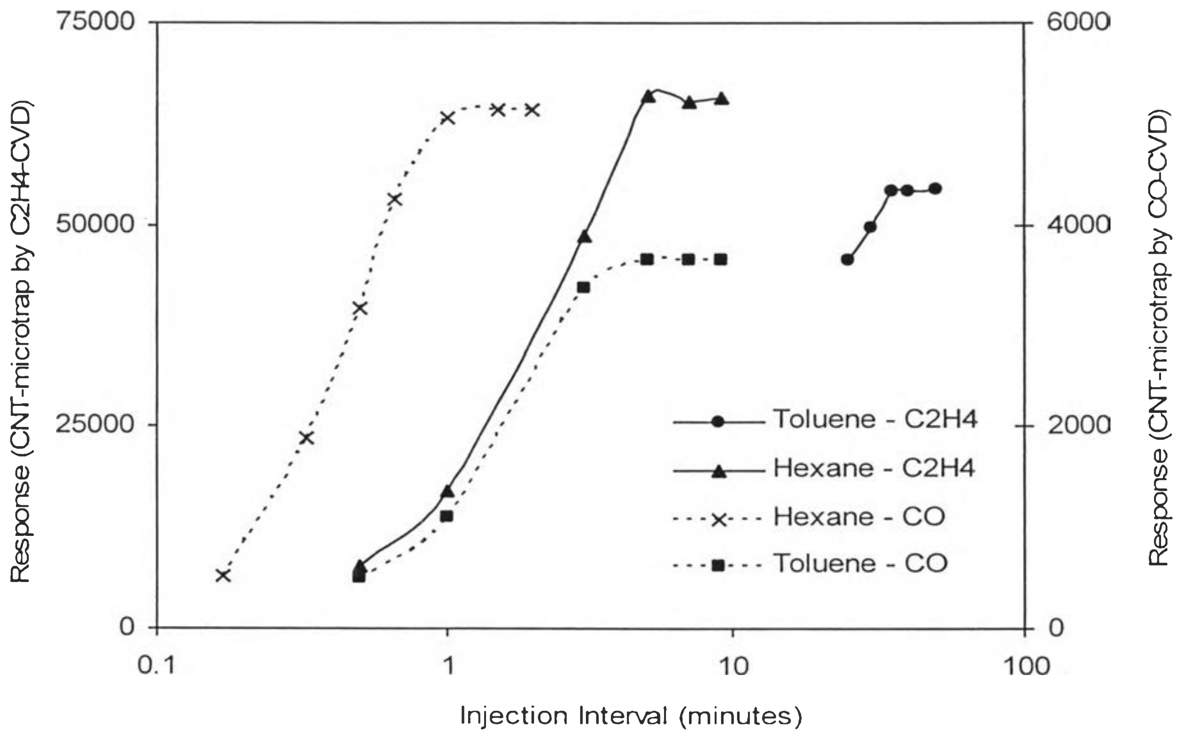


Figure 4.5. Detector response as a function of injection interval using CNT microtrap made by CO and C_2H_4 CVD. The flow rate was 7 ml/min. The dotted line represents data by CO-CVD, and the bold line by C_2H_4-CVD.

4.4 Conclusion

The self-assembled multiwall CNTs were formed by CVD on the inside wall of stainless steel capillaries, with the iron in the steel serving as the catalyst for nanotube growth. This relatively simple approach can be applied to CNT-based devices for chemical processing and analytical sensing, where the CNT film provides an active surface for adsorption/desorption of organic molecules. The CNT film in the capillary showed high adsorption as well as fast desorption of small organic molecules, such as, hexane and toluene. The film made by C_2H_4-CVD showed higher CNT density and thus, higher sorption capacity. The sorption of toluene was much stronger than hexane, which is attributed to the π-π interaction between the CNT sidewall and the aromatic ring of toluene. Fast desorption (measured as 1.4 sec. bandwidth at half height) is an important feature for adsorption and sensing applications.