CHAPTER 3

DEVELOPMENT OF CONTINUOUS ON-LINE PURGE AND TRAP

3.1 Introduction

Measurement of trace organics in water consists of isolating the organics prior to analysis by Gas Chromatography (GC) or Gas Chromatography Mass Spectrometry (GC-MS). Common sample preparation techniques for volatile organics include purge-and-trap (P&T) [2,3,28,29], head space analysis (HS) [2,3,26,27], and solid phase microextraction (SPME) [2,3,30]. All these established methods provide excellent analytical results and have their advantages and disadvantages. However, they are predominantly laboratory methods and can not be used for on-line, real-time (or near real-time) monitoring.

Purge and trap is the most widely used method for the analysis of trace volatile organics in water [31-33]. Many Standard EPA methods are based on Purge and Trap, and it is widely used in industry [2]. Here, an inert gas (e.g. N_2) purges the organics from the water into a gas phase, which are then concentrated on a sorbent trap. Subsequently the organics are thermally desorbed and injected into a GC or a GC-MS. It offers an improvement over static headspace extraction, and is often referred as the dynamic head space analysis. It has high sensitivity and is suitable for quantitation of a large number of compounds.

The purge and trap system consists of two major components: a purging device and a sorbent trap. Several purge chamber designs are commercially available. Typically, several milliliters of water is placed in the chamber. Then the purge gas is turned on for exhaustive extraction. The extraction efficiency is effected by the properties of the analytes, the temperature, the flow rate, and the purge duration. The sensitivity is

improved by elevated temperature, optimum flow rate and longer purge time. The trap consists of a one or more (typically 3) commercial sorbents. It is designed to retain all of the purged organics, thus breakthrough needs to be eliminated. This is often achieved by using a lower trap temperature and selecting suitable sorbents. Desorption efficiency is affected by trap temperature, heating rate and desorb-gas flow rate [34]. The maximum desorption temperature is limited by the thermal stability of the sorbent material. For most analytes, the detection limits are at ppb to ppt level. Conventional sorbent traps used in purge and trap tend to be relatively large (2- 4 mm ID), and can not be desorbed rapidly. A second trapping stage is normally used to provide injection for GC separation.

On-line monitoring offers several advantages. They provide better quality data at a lower cost, and eliminate errors introduced during sampling and laboratory handling [36,37]. On-line methods also provide real-time information that can be used for process control [16,36]. Consequently, there is much interest in continuous monitoring of organics in drinking water, industrial waste water, ground water, process water and in safeguarding water reservoirs for homeland security. Several methods have been developed for on-line water monitoring. Some of them use membranes for selective extraction of analytes. Examples include membrane introduction mass spectrometry (MIMS) [39-41] and gas injection membrane extraction (GIME) [43]. In MIMS, a selective membrane interfaces the water sample to the vacuum in the ionization chamber, thus the organics permeate directly into the MS. However, direct mass spectrometry is not suitable for complex mixtures. In GIME, membrane extraction is interfaced with a GC. The process is speeded up by using a gas to inject the sample.

Continuous extraction and a faster acting sorbent trap are needed to develop a continuous purge and trap system. A microsorbent trap, referred to as a microtrap, has been developed as an on-line sample preconcentration and injection device for

continuous, on-line monitoring of low level organics [7,9,11,12]. It has been used in both air and water monitoring. It is a short, small diameter (0.25 to 0.5 mm ID) trap with low heat capacity; allowing it to be heated or cooled rapidly. Fast heating provides narrow injection band, while fast heating-cooling cycle leads to faster operation. As the sample flows into the microtrap, it accumulates the organics on the sorbent while the background gases pass through. Resistive heating using a pulse of electric current makes an injection for GC separation (or GC-MS) by rapidly desorbing the retained organics. Continuous monitoring is achieved by making a series of injections at short intervals, which generate a series of chromatograms. The microtrap has been used as a stand-alone device, or in conjunction with a gas sampling valve [7,10,13]. Such devices have shown several advantages, for example, they are simple, can be operated automatically in on-line monitoring, yield low detection limits and can handle relatively large concentration of moisture [16,17].

The objective of this study is to develop an on-line purge and trap system for continuous water monitoring. The purging is carried out continuously while the microtrap is used for on-line concentration and injection.

3.2 Experimental

The schematic diagram of the experimental system is shown in Figure 3.1. It consisted of three sections, namely separation, preconcentration and analysis. The separation was carried out in an on-line purge chamber, while the purged organics were concentrated in a microtrap system. The analysis was carried out by GC-FID. The water sample flowed continuously (FMI Lab Pump Model RP-G 150) into the purge chamber and exited through an outlet tube. The stripping gas (N_2) also flowed continuously

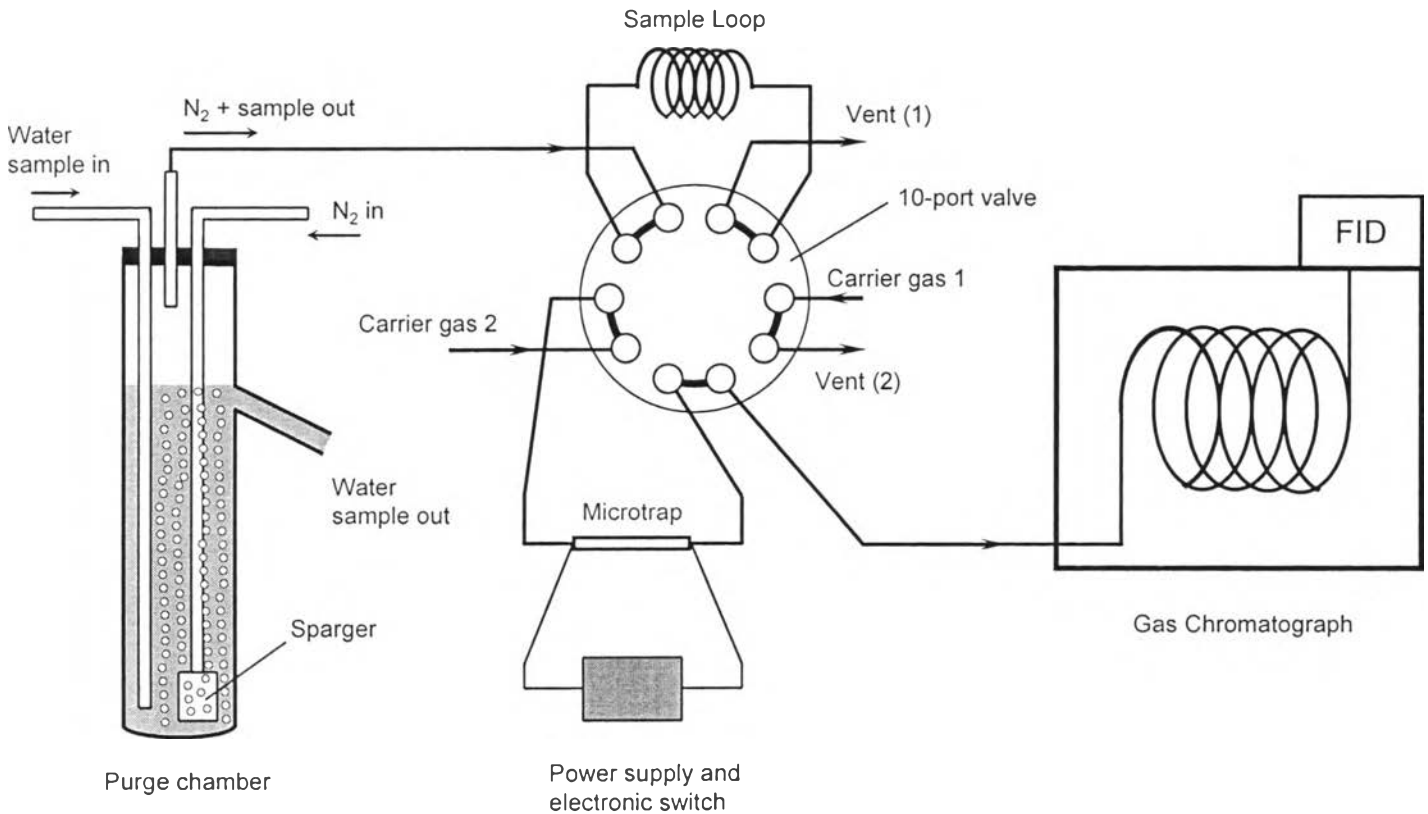

Figure 3.1. Schematic diagram of the experimental system.

through a frit spargers designed to disperse the N_2 into small bubbles for efficient gas-liquid contact as shown in Figure 3.2. The effluent gas moved into the concentration/injection section. A large volume injection was necessary to obtain low detection limits. A gas sampling valve with a large injection loop was used in series with the microtrap. The analytes were concentrated by the microtrap before making a sharp GC injection. A ten-port valve (Valco Instrument Co.Inc., Houston, TX) was used here.

The valve and the microtrap were configured for continuous, on-line analysis as shown in Figure 3.3. In the loading position, effluent from the purge chamber flowed through the sample loop, while the carrier gas 2 (He) flowed through the microtrap and onto the GC. During this time, the microtrap was heated with a pulse of electric current to desorb/inject the analytes into the GC. Then the valve was switched to its injection position, carrier gas 1 (He) transferred the contents of the sample loop to the microtrap, while carrier gas 2 flowed through the GC column.

The microtrap was connected directly to the GC column and served the functions of preconcentration and an injection. It was made by the packing approximately 20 mg of 60/80 mesh Carbotrap C (Supelco, Bellefonte, PA, USA) in a 15 cm × 0.53 mm ID thin fused silica lined stainless-steel tubing (HTX-16TW, Small Part Inc., Miami Lakes, FL). It was connected to a variable power supply (Variac, SATCO Energy Product) which could provide 7-10A of current. The microtrap was resistively heated by passing a pulse of electric current directly through the wall of metal tubing.Typical trap temperatures were of the order of 300-400 °C [13]. A microprocessor controlled timer fabricated in house was used to control the interval between injection and the duration of microtrap pulse. This is shown in Figure 3.4.

Analysis was carried out using a Hewlett-Packard gas chromatograph (Model 5890 series II) equipped with a flame ionization detector (FID). A 60 m × 0.25 mm

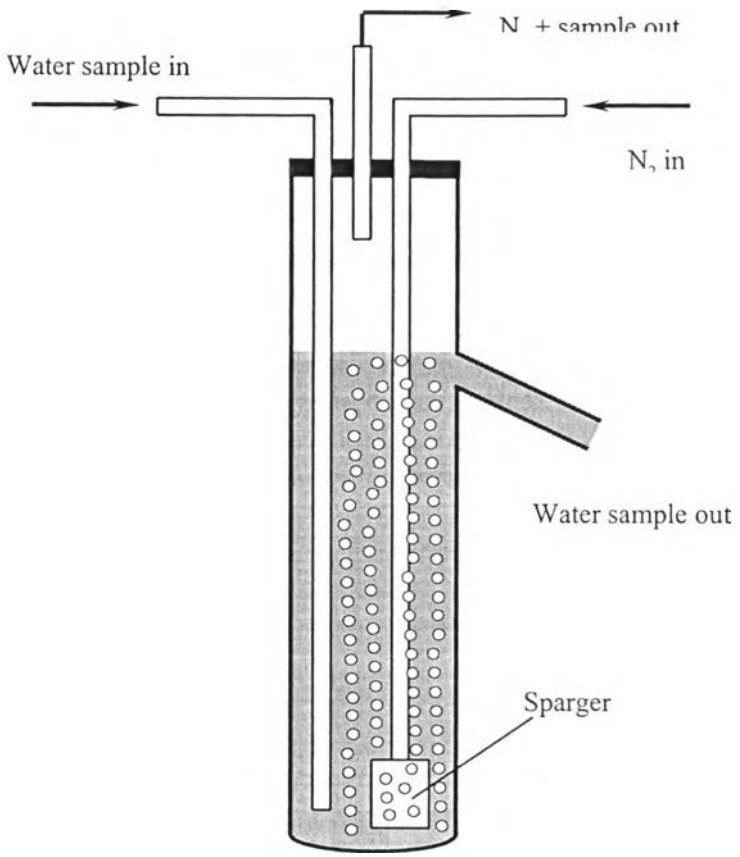

Figure 3.2 Schematic diagram of the continuously purge chamber

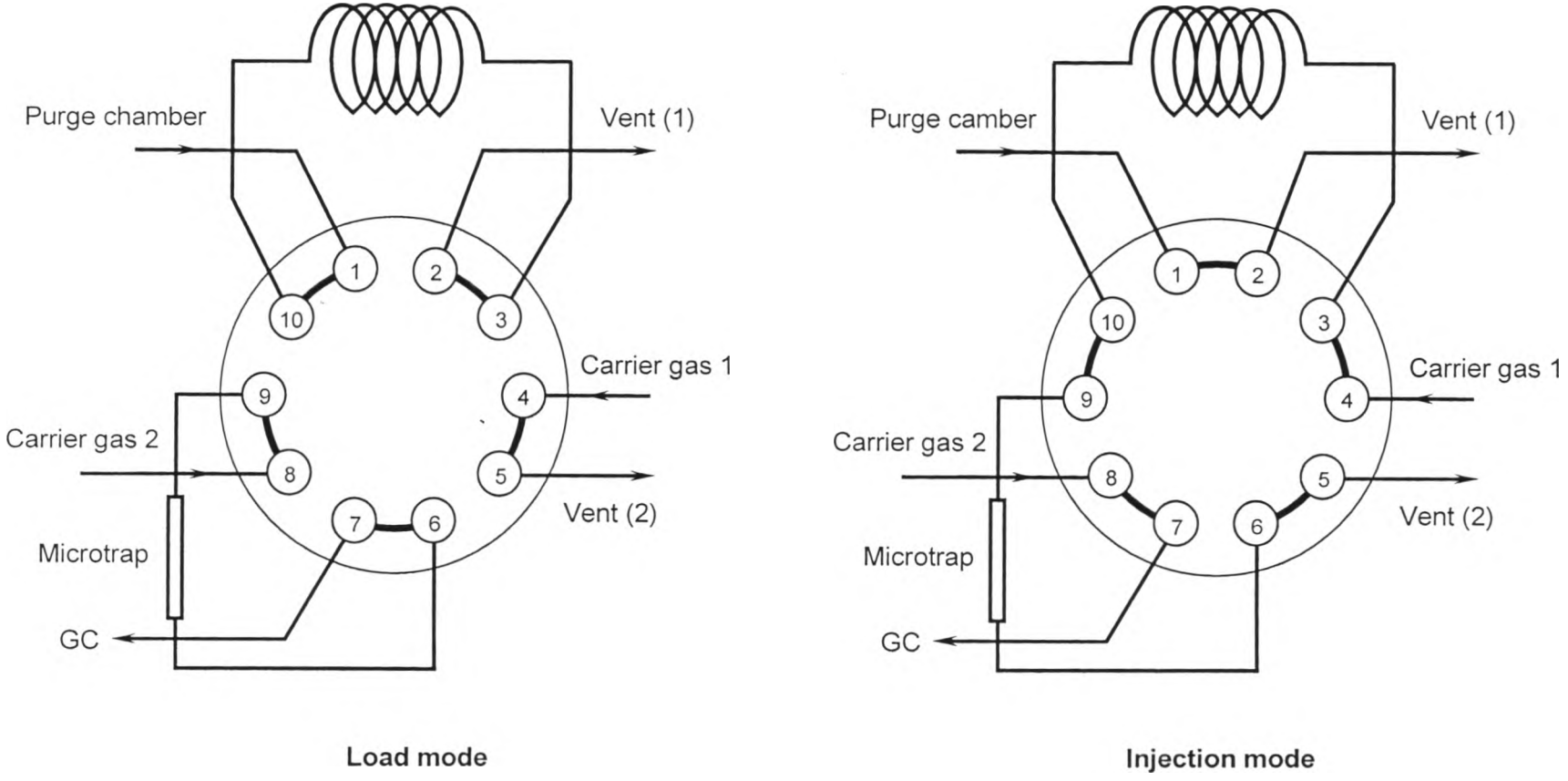

Figure 3.3. Schematic diagram of the ten-port valve connections.

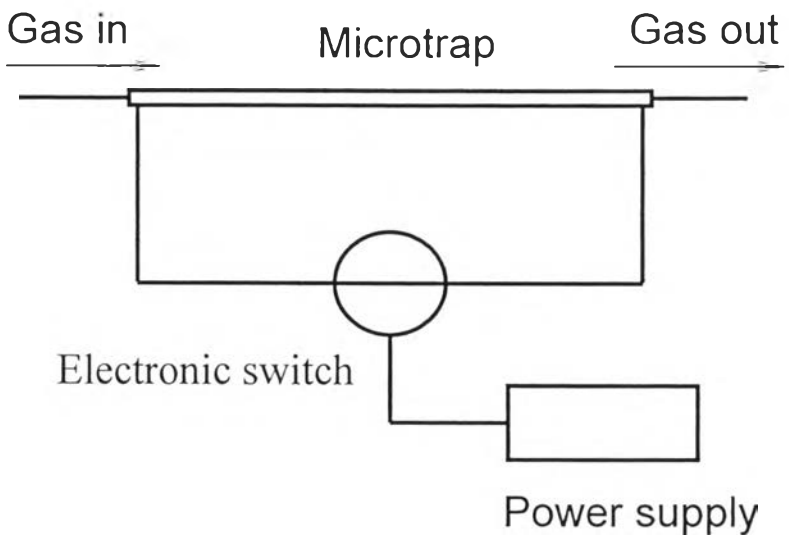

Figure 3.4 Schematic diagram of microtrap connect with microprocessor control timer

ID DB-1 megabore column with a 3 μm stationary phase (J&W Scientific, Folsom, CA, USA) was used for separation. Hewlett-Packard 3365 Chem Station was used for data acquisition and analysis. Nitrogen was used as the stripping gas while helium was used as the carrier gas (Matheson Gas Co., East Rutherford, NJ). The chemicals used in this experiment were analytical grade (Sigma Chemical Co. St, Louis, MO). All samples were prepared with methanol and distilled water.

3.3 Results and Discussions

The focus of this study was to develop a continuous, purge and trap system. The purge chamber was designed so that water could continuously flow in and out. At a given flow rate, the volume of the purge chamber determined the residence time.

The purged organics were preconcentrated prior to GC injection. In conventional purge and trap, the organics are concentrated from the whole purge volume. While this provides a lower detection limit [33], it is also a slow process. A faster injection system comprising of a valve and a microtrap was used here. The sample loop size determined the volume of purged gas from which the organics were concentrated. The sample loop volume could be varied. A large loop size required longer fill up time, but lowered detection limits.

A 3 ml sample loop was used in this study, although injection volume as large as 40 ml has been employed before [17]. In the loading position, the sample loop was filled with the gas from the purge chamber, while the excess gas was vented out. Then the valve was switched to the injection position where carrier gas removed the analytes from the sample loop, and injected into the microtrap. This step took approximately 70 seconds to complete. Based on microtrap breakthrough data published previously [15,17], no analyte

breakthrough was expected. Then the valve was switched back to the loading position and the microtrap was desorbed by applying an electric pulse. Continuous purging was combined with repeated microtrap injection to facilitate near-real time monitoring.

3.3.1 Theoretical Considerations

Purging organics out of water can be approximated as partitioning between the water and the purge gas. The mass balance may be presented as:

$$C_0 V_w = C_w V_w + C_g V_g \qquad (1)$$

where C_0 is the initial concentration of the analyte in water, C_w is the equilibrium concentration of the analyte in water, C_g is the equilibrium concentration of the analyte in the purge gas, V_w is the volume of water exposed, and V_g is the volume of gas purged through the water.

The Henry's law constant, H, which is the ratio of concentrations of the analyte in gas and the aqueous phases is given in its unitless form as $H^* = C_g/C_w$, or as $H = H^*/RT$, where H is in atm-m^3/mol. Solving the Equation (1) for C_g it yields:

$$C_g = \frac{C_0}{\frac{RT}{H} + \frac{V_g}{V_w}} \qquad (2)$$

Here the volume of water, V_w, and the volume of purged gas, V_g, can be expressed as $V_w = F_w \tau$ and $V_g = F_g \tau$, where F_w, F_g are the flow rates of water and gas respectively, and τ is purge residence time, i.e. the time during which the gas- liquid phases contact occurred. So, Equation (2) can be written as:

$$C_g = \frac{C_0}{\frac{RT}{H} + \frac{F_g}{F_w}} \qquad (3)$$

The Henry's constant, H, can be expressed as a function of temperature [27] as:

$$H = e^{A-\frac{B}{T}} \tag{4}$$

where A and B are constants, and T is the absolute temperature. Combining Equations (3) and (4), the concentration of an analyte in the gas phase is given as:

$$C_g = \frac{C_0}{\frac{RT}{e^{A-B/T}} + \frac{F_g}{F_w}} \tag{5}$$

Equation (5) was used to simulate the concentration of the analyte in the purge gas. Higher analyte concentration in gas leads to the accumulation of larger amounts of analytes in the microtrap, and consequently to higher detector response, S. This was calculated as:

$$S = C_g \times V_{inj} \times f = \frac{C_0}{\frac{RT}{e^{A-B/T}} + \frac{F_g}{F_w}} \times V_{inj} \times f \tag{6}$$

where, V_{inj} is the volume of the sample loop, and f is the response factor. According to equation 6, the system response is a function of the flow rates of water and N_2, and the operating temperature. It can also be increase by increasing the volume of the sample.

3.3.2 The Effect of Process Variables

Purge chamber volume: The purge chamber volume was an important variable that affected extraction efficiency and sensitivity. In this study, the volume was varied between 8 to 25 ml. A larger chamber contained more water, thus making more analytes available. However, it also required a larger sample size and higher N_2 flow rates. Figure 3.5 shows the signal response as a function of volume of the purge chamber, when the water and the N_2 flow rates were fixed at 10 ml/min and 3 ml/min respectively. First, the

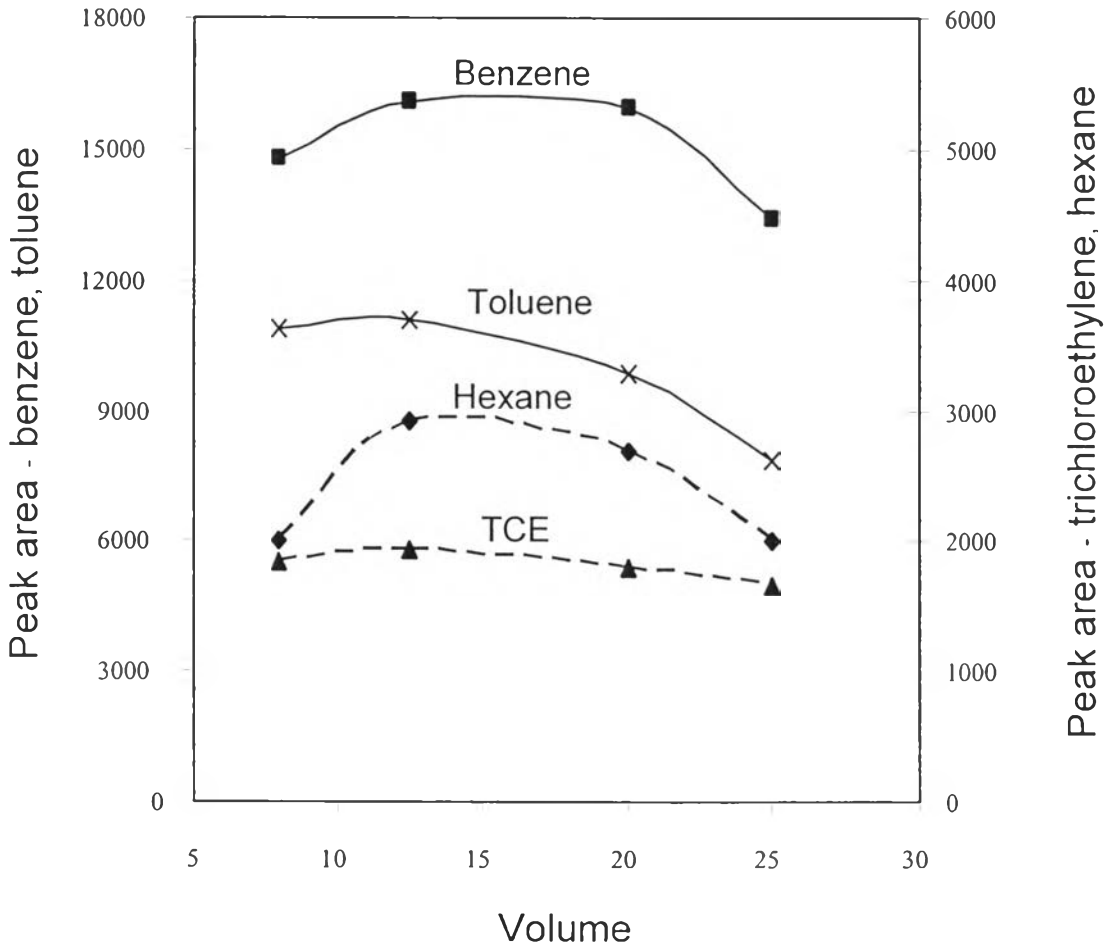

Figure 3.5 Peak area as a function of the purge chamber volum The water and N_2 flow rates were 10 and 3 ml/min respectively.

response increased with the volume of the purge chamber, and then it decreased. The increase is attributed to larger water residence time, and the decrease was due to lower purge efficiency when the volume was too large. This demonstrates that at a fixed gas to water flow rate ratio, there is an optimum purge chamber volume.

The effect of water flow rate: The water flow rate was varied between 1 to 10 ml/min. The purge rate and the purge chamber volume were fixed 3 ml/min and 12.5 ml respectively. As shown in Figure 3.6, the response increased with the increase in water flow rate. Higher water flow rate brought more analytes into the purge chamber, thus increasing the mass of analytes purged into the gas phase resulting in a higher response. This trend is also predicted by equation 6. The response was computed as a function of water flow rate using this equation, and is plotted in Figure 3.6. The model predicted the system response quite effectively.

Nitrogen flow rate: The effect of nitrogen flow rate is shown in Figure 3.7. Initially, the response increased with the increase of nitrogen flow rate. Higher N_2 flow rate increased the amount of anlytes purged out from the water. When nitrogen flow rate was increased further, the response decreased. This is because the higher flow rate diluted the organics in the purged gas. Since the injection volume was fixed, a dilute gas stream resulted in reduced sensitivity.

According to equation 6, as the flow rate of the purge gas increases, the system response should decrease. In the rising section of 4, the flow rate was so low that equilibrium was not reached. As the flow rate increased, the equilibrium conditions were reached and the response begin to drop according to equation 6.

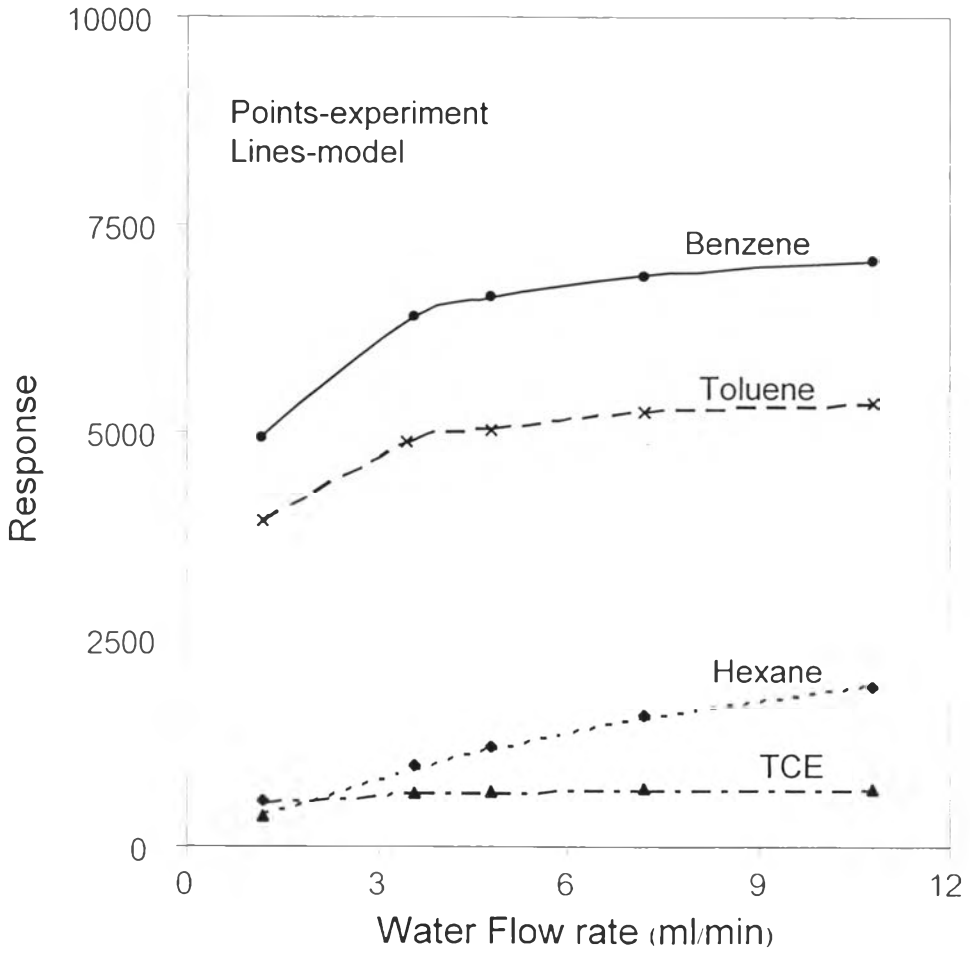

Figure 3.6 Detector response as a function of sample water flow rate (N_2 – 3 ml/min, chamber volume – 12.5 ml).

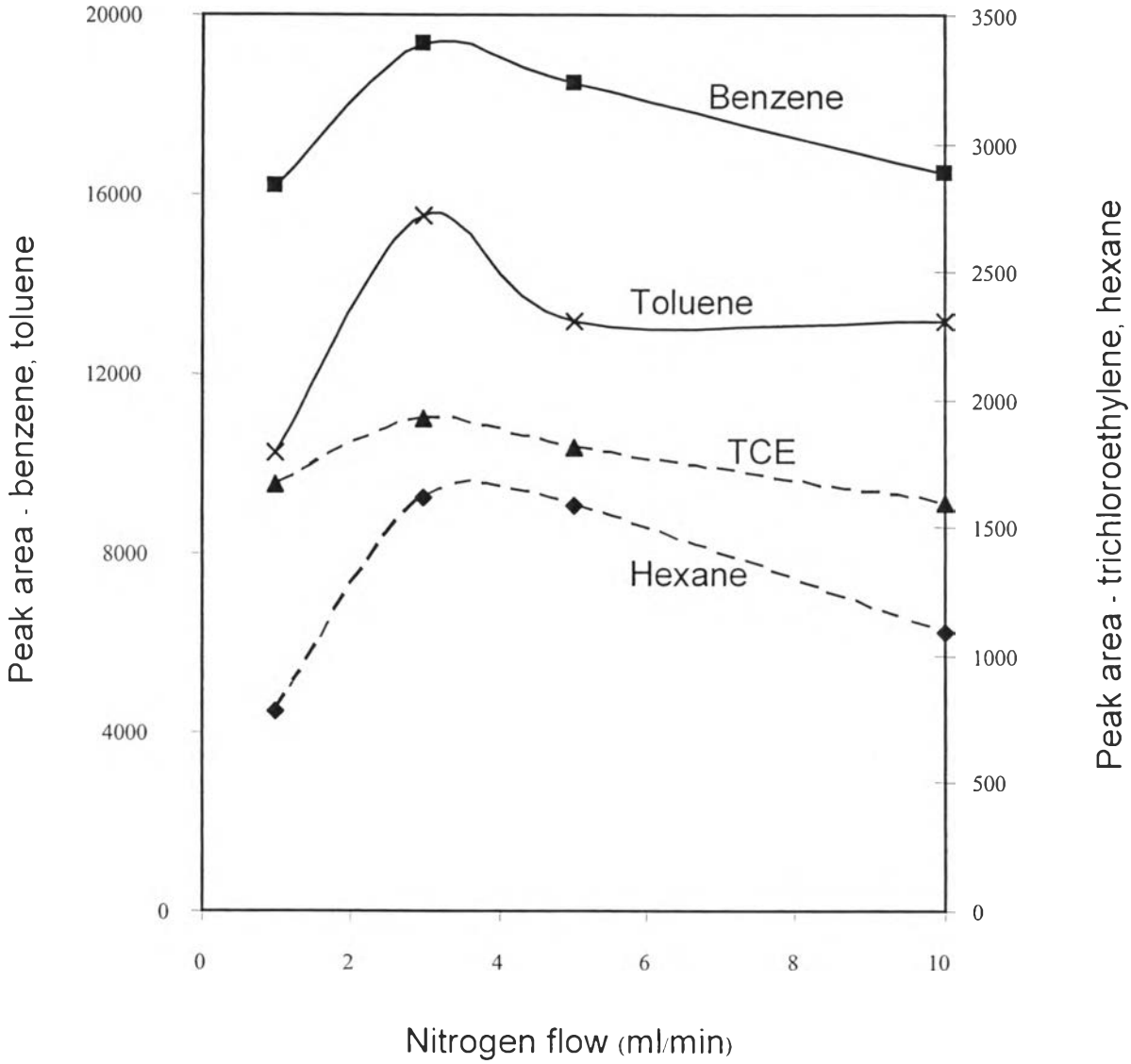

Figure 3.7 Peak area as a function of nitrogen flow rate(water – 10 ml/min, chamber volume – 12.5 ml).

Loading Time : The time when carrier gas pushed the analytes out of the sample loop to inject into the microtrap also affected the system response. Its referred to as the loading time. Its effect are shown in Figure 3.8. It took 70 second to purge all the analytes out of the 3 ml sample loop. This appered to have some effect on sensitivity, and depended on the injection volume.

Effect of temperature: The system response was studied as a function of temperature (25° to 60°C) with a water sample containing 1 ppm each of hexane, benzene, trichloroethylene and toluene. The experimental data and the model simulation are plotted in Figure 3.9. As shown, the detector response increased with increase in water temperature. This trend was expected according to equation 6. For a given analyte, the increase is a function of the constants A, and B [48], which varies from compound to compound. The response for high vapor pressure and lower molecular weight compounds, such as, hexane and benzene increased nearly three times with the increase in temperature. The increase in response for toluene and trichloroethylene were relatively lower. Simulation using equation 6 was able to predict the experimental data of Figures 3.6 and 3.9 quite well.

Extraction Efficiency (EE) is defined as the fraction of analytes extracted, and is computed as:

$$\mathrm{EE}(\%) = \frac{C_0 - C_{out}}{C_0} \times 100\%$$

where C_0 is the initial analyte concentration in the water sample, and C_{out} is the concentration in the exit stream. Higher EE are desirable as they lead to higher sensitivity and precision.

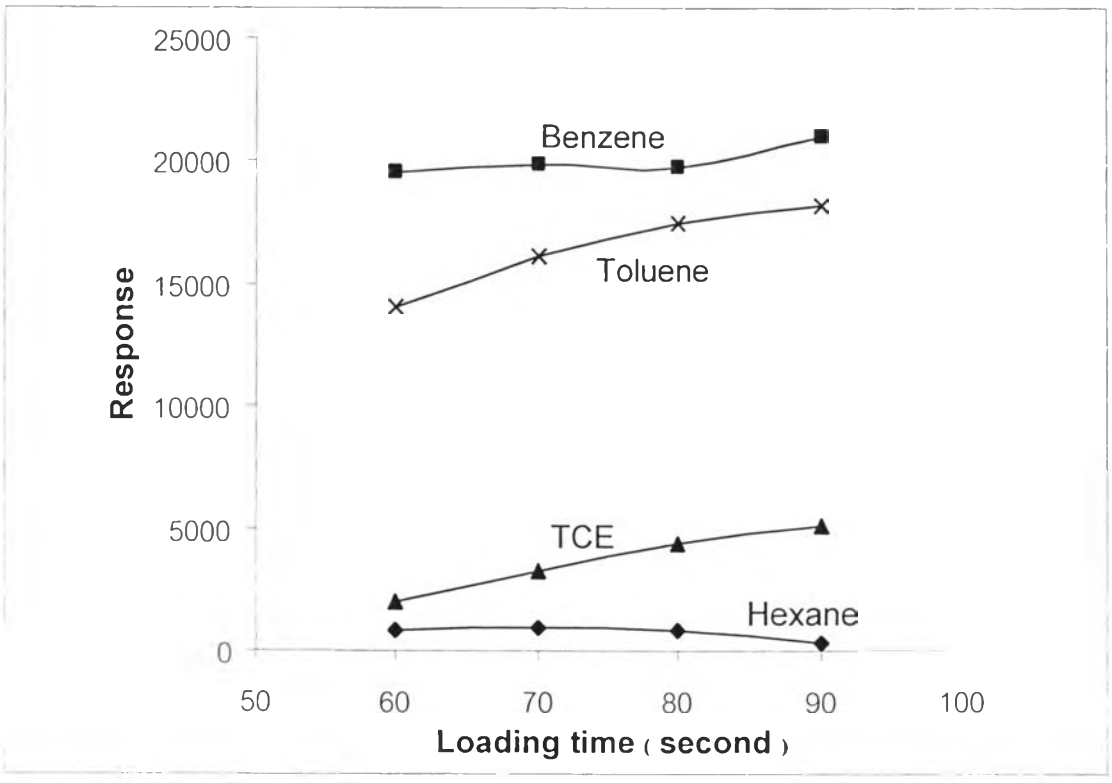

Figure 3.8 Detector Response as a function of loading time The water and the N2 rates were 10 and 3 ml/min respe flow ctively

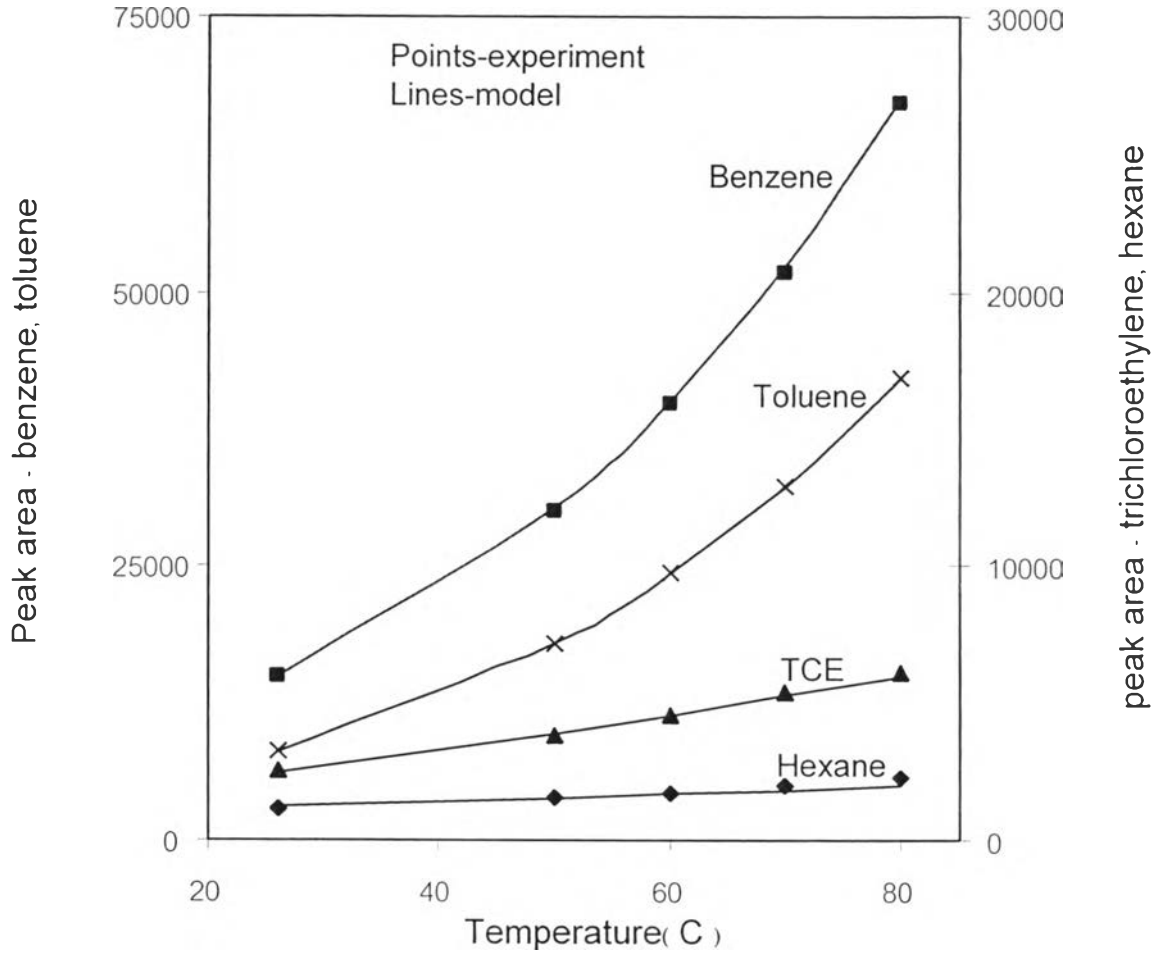

Figure 3.9 Peak area as a function of the sample water temperature (N_2 – 3 ml/min water– 10 ml/min, chamber volume – 12.5 ml).

EE depends upon the properties of the analytes, purge temperature, flow rate, purge chamber volume and residence time. Higher valves of temperature, purge flow rate and residence time increased extraction efficiency [34]. At 60°C, the EE was above 80 % for all the compounds studied here. This is shown in Table 3.1.

Table 3.1. Extraction Efficiency (%) as a function of temperature of the water sample.

Temperature, °C	Hexane	Benzene	Trichloroethylene	Toluene
25	15	21	43	43
50	78	75	84	89
60	81	80	87	92

3.3.3 Analytical Performance

The analytical performance was tested with a 12.5 ml purge chamber, and a 3 ml gas injection sample loop. The water flow rate and the nitrogen flow rate were 10 ml/min and 3 ml/min respectively. The column temperature was programmed from 30°C (6 min) to 120°C (3 min) at 25°C/min,so that the separation was completed in 10 min. The chromatographic run could be shortened using narrower bore column. No special attempts were made to decrease the analysis time. The cycle time of the valve-microtrap injection system was about 70-75 sec. So, the analysis time here was limited by the GC separation. The typical sequence of chromatogram is shown in Figure 3.10.

Linear calibration curves were obtained for all the analytes in the concentration range of 50 ppb to 1 ppm as shown in Figure 3.11. The regression coefficients for hexane, benzene, trichloroethylene and toluene were 0.9896, 0.9998, 9919 and 0.9907 respectively. The precision expressed as percent relative standard deviation (% RSDs) in peak area for hexane, benzene, trichloroethylene and toluene were 2.6, 0.7,4.9 and 1.7

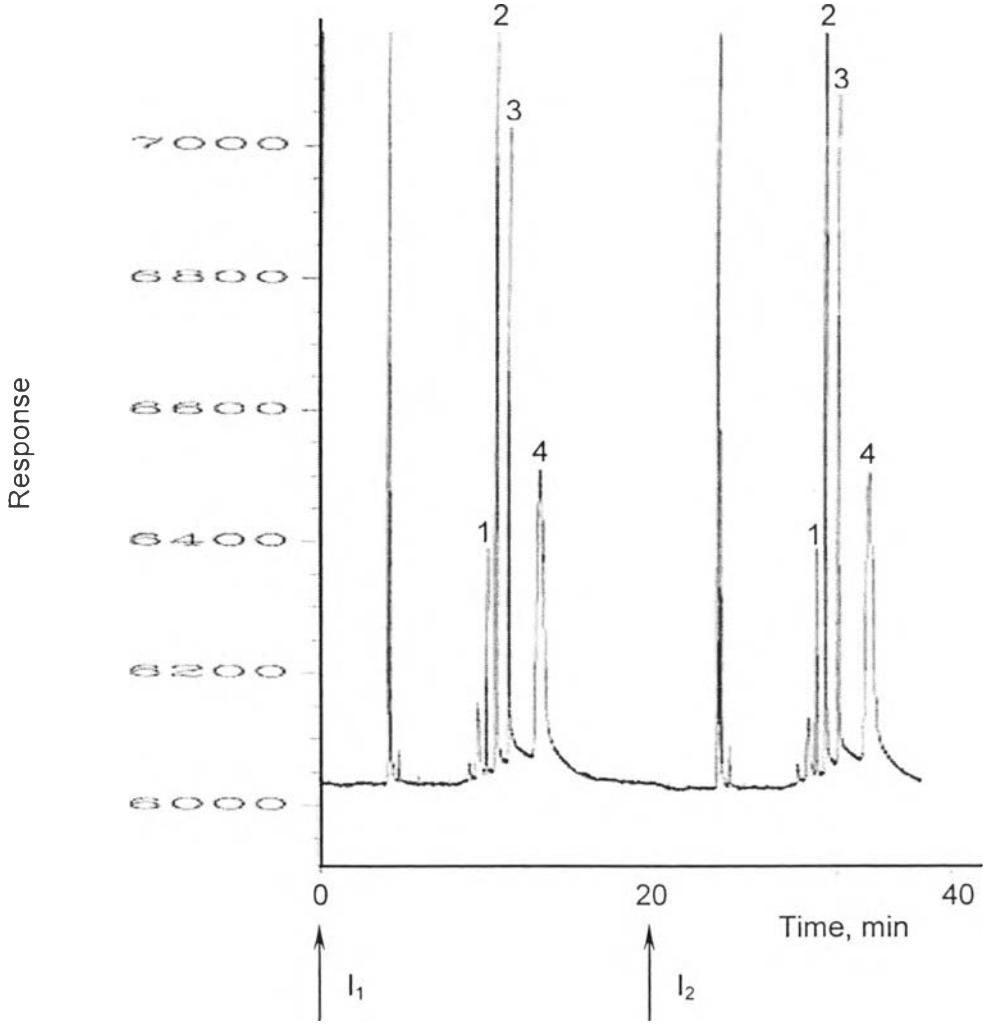

Figure 3.10 Series of chromatograms generated during continuous monitoring. Injections were made every 20 min at points I_1, I_2,...(1 – hexane, 2 – benzene, 3 – trichloroethylene, 4 – toluene).

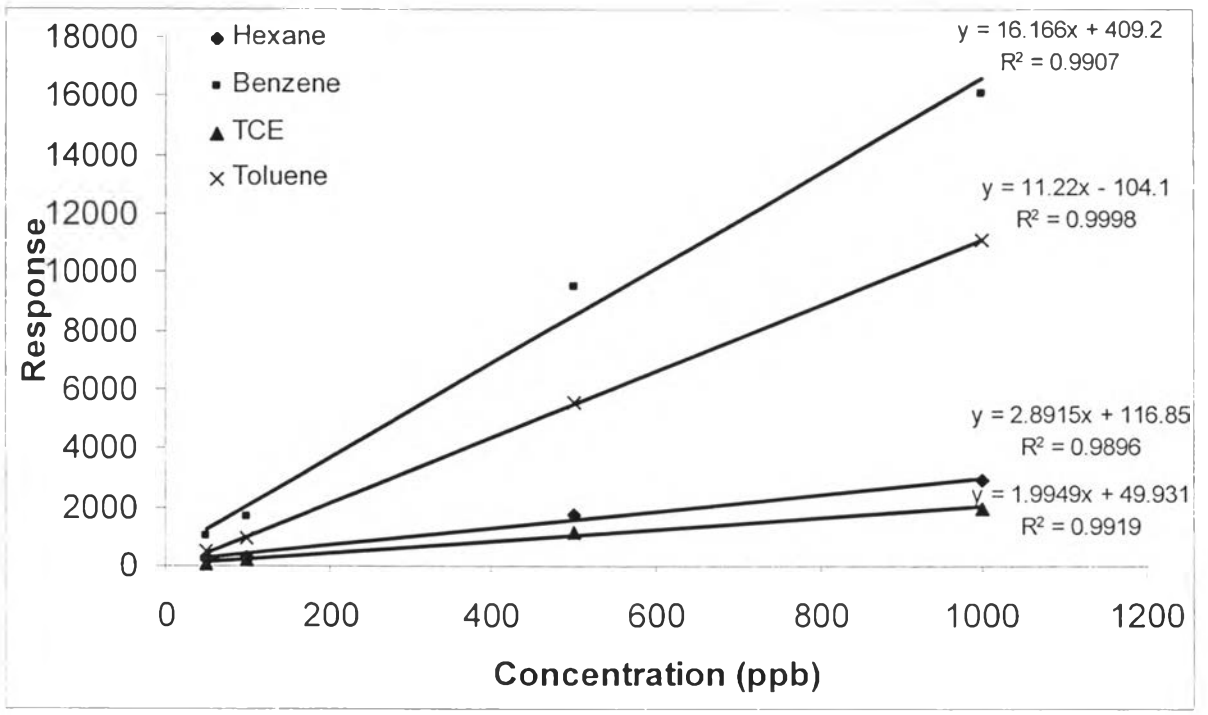

Figure 3.11 Calibration curve of hexane benzene trichloroethylene and toluene measured by continuous on-line purge and trap

respectively. The Method Detection Limits (MDLs) for hexane, benzene, trichloroethylene and toluene were 31.8 ppb, 2.6 ppb, 56.2 ppb and 4.2 ppb respectively. The MDLs were calculated using a standard EPA method [28]. This system could achieve low detection limit if the sample loop volume was increased. The detection limit also depended on the other operating parameters mention before.

In order to ensure system stability during long periods of operation, a water sample containing benzene was analyzed continuously for 10 hours. The response over this period is shown in Figure 3.12. The response was found to be stable and the relative standard deviation over this period was 8.3 %.

3.4 Conclusion

A continuous purge and trap, which interfaced continuous purging with a microtrap injection system was developed. It was able to monitor volatile organics at ppb levels. The system exhibited good reproducibility, long-term stability and low detection limit. The system response was a function of flow rate, purge chamber volume and temperature. A predictive model was developed based on gas-liquid partitioning of the organics. This was found to describe the experimental data quite well and could be used to predict system performance.

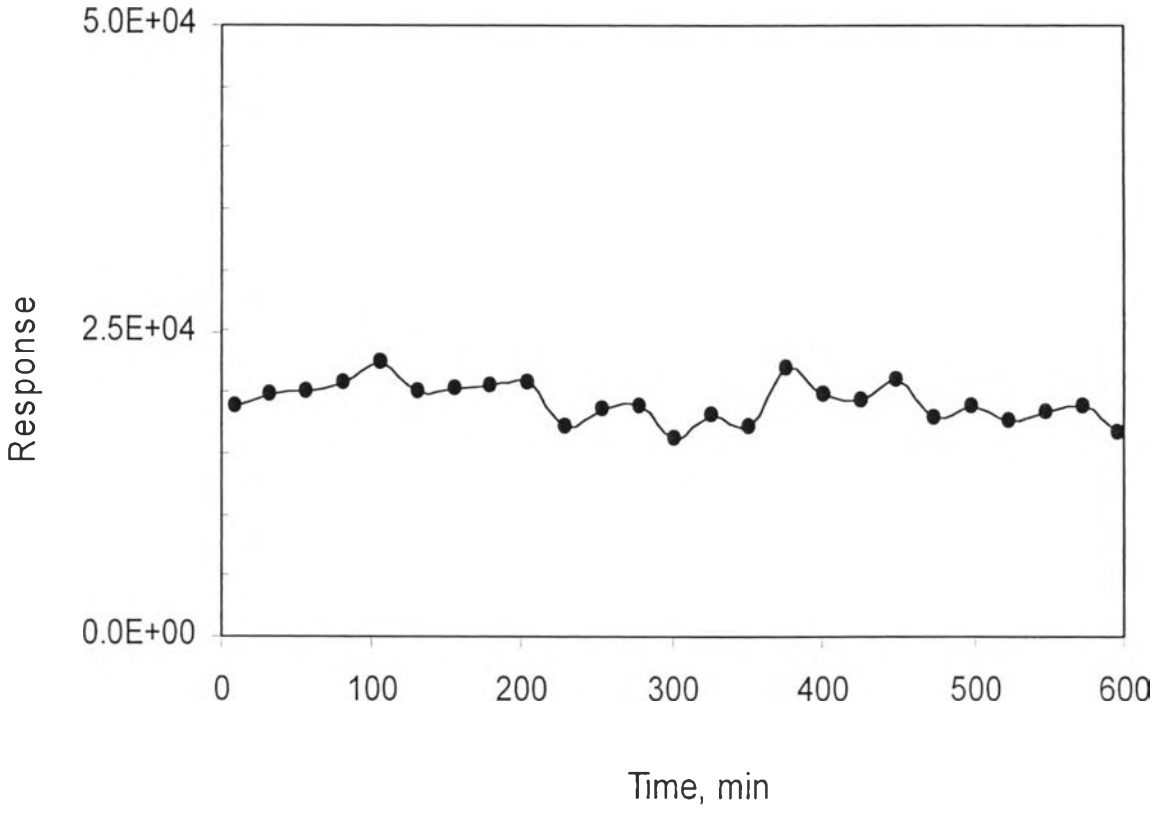

Figure 3.12 Long term stability of the dynamic purge and trap system.