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ABSTRACT

CONTINUOUS MONITORING OF VOLATILE ORGANIC COMPOUNDS USING MICROTRAP BASED GAS CHROMATOGRAPHIC SYSTEMS

by
Yonghua Xu

Continuous analysis allows a representative portion of a sample to flow continuously through an analytical instrument, which gives analytical information with little or no delay in time. A microtrap is a small diameter tube packed with adsorbents in series. When a gaseous sample containing volatile organic compounds (VOCs) flows through the microtrap, the VOCs can be trapped selectively by adsorbents. Then a pulse of electrical current is applied to the microtrap. This rapid heating results in a desorption that can act as a sharp injection for GC separation. Thus the microtrapped sample is the total amount of VOC present in the sample stream during the time period between two sequential injections.

Three injection systems: the gas sampling valve, the sequential valve microtrap (SVM) and the on-line microtrap-backflushing system (OLMT-BF) were compared for response characteristics and detection limits. Both SVM and OLMT-BF systems were shown to have low detection limits, and the OLMT-BF system can obtain information almost continuously even during the time period between the pulses. A microtrap based nonmethane organic carbon (NMOC) analyzer was also developed for continuous monitoring of a gas stream. In the NMOC analysis, the microtrap served to separate all permanent gases from the organics as well as an on-line preconcentrator for NMOC. The microtrap based NMOC analyzer has low detection limits and low interference from CO_2 and H_2O.

A method for continuous monitoring of VOCs in water has been developed using on-line membrane extraction and microtrap GC system. Aqueous sample containing VOCs is passed through a hollow fiber membrane. The VOCs

selectively permeate across the membrane into an inert gas stream. The VOCs are concentrated and injected into GC column using the microtrap. Continuous monitoring is achieved by making a series of injections.

A minitrap-canister system has been studied for analysis of VOCs in ambient air. An ambient air sample was collected in a Summa canister. Then the sample was concentrated using a multibed minitrap. The trapped VOCs were released rapidly by an electrical pulse and injected on to a GC column without any focusing. The detection limits for hexane and toluene are 0.02 ppb.

CONTINUOUS MONITORING OF VOLATILE ORGANIC COMPOUNDS USING MICROTRAP BASED GAS CHROMATOGRAPHIC SYSTEMS

by
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A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

Department of Chemical Engineering, Chemistry
and Environmental Science

May 1996

APPROVAL PAGE

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To my mother and brothers who provided the opportunities, and to my wife, Wenjun, and my son, Chentong for their love, patience, and understanding.

ACKNOWLEDGMENT

I would like to express my deepest appreciation with most sincere gratitude to my advisor Dr. Barbara Kebbekus, who not only served as my research advisor, providing valuable and countless resources, insight, and intuition, but also gave me moral support, encouragement, and understanding throughout this research. I would also like to thank Dr. Somenath Mitra for his guidance and support during the first two years research in his group. Special thanks to Dr. Joseph Bozzelli, Dr. Richard Trattner and Dr. Pradyot Patnaik for serving as members of the committee.

I would like to thank Dr. Gordon Lewandowski, Dr. Richard Trattner and Dr. Ronald Kane for their understanding, support, and encouragement in the completion of my doctoral degree. I also wish to express my appreciation to Ti-Wu Wang Foundation, who provided financial support in my first academic year.

Many thanks also go to Mrs. Maria DaRocha, Dr. Constantinos Nicolaou and my colleagues at Sun Chemical Corporation for their understanding, encouragement and support.

I am grateful to Wenjun Chen, my wife for her support during the entire course of this research. I would like to thank my mother-in-law, who was taking care of my son so that I could have enough time to finish my research.

Financial support from Atmospheric Research and Exposure Assessment Laboratory of US EPA, Office of Air Quality Planning and Standards of US EPA, Hazardous Substance Management Research Center at NJIT is acknowledged.

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CHAPTER 1

INTRODUCTION

1.1 Analysis of Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) on the list of 189 Hazardous Air Pollutants in the 1990 Clean Air Act Amendments include a variety of straight chain, aromatic hydrocarbons, as well as organic compounds containing different functional groups. VOCs cover the compounds which have boiling points well below ambient temperature such as vinyl chloride, propane and acetylene, as well as those which are volatile chemicals at room temperature, such as toluene, trichloroethylene and ethanol. The US EPA (United States Environmental Protection Agency) Methods 601 and 602 list more than thirty volatile organic compounds as primary interest pollutants. These VOCs in the environment may escape or be discharged from chemical processes, incident spills and the exhaust gases of motor vehicles. Generally, there are two categories of pollutant sources: stationary and mobile. Thus chemical plant and landfill sites are stationary sources and the automobile is an example of a mobile source. The presence of VOCs in air and water is a public concern because many of the organic compounds are toxic and/or carcinogenic. Furthermore, VOCs in water eventually evaporate into air as air pollutants to generate ozone and smog by a series of photochemical reactions.

VOCs are important atmospheric constituents from both a chemical and biological standpoint. Figure 1 summarizes some of the significant atmospheric functions of volatile organic compounds [1]. VOCs are one of the primary ingredients in the chemical process that produces smog on an urban and regional scale. For example, VOCs can react with NO_x under sunlight to generate aerosol homogeneously and ozone, which may be harmful to the lung and respiratory system. VOCs influence atmospheric acidity because products of their oxidation, such as peroxy radicals, facilitate the oxidation of sulfur and nitrogen oxides to

sulfuric and nitric acid. Organic acids generated from atmospheric photochemical reactions contribute to the lowering of pH in acidic desorption processes.

On a global scale, VOC oxidation leads to products such as CO_2 and O_3, which absorb outgoing radiation and thus can contribute to climate warming. Carbon monoxide, which is a product of VOC oxidation, is not a primary greenhouse gas. However, it can affect climate change indirectly through its reaction with atmospheric hydroxyl radical. Increases in CO will reduce ·OH levels, which in turn will lead to an increase in atmospheric methane concentrations, because ·OH is the major sink for methane. Methane is one of the more important greenhouse gases in the troposphere.

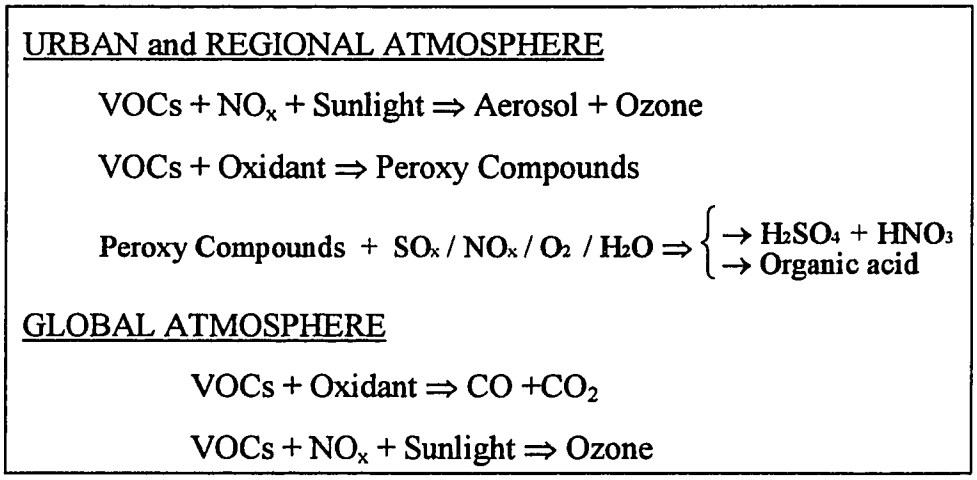


Figure 1 The role of VOCs in atmospheric chemistry

The conventional Environmental Protection Agency (EPA)-approved methods of collection and analysis of organic compounds in air and water consist of obtaining a grab sample, transporting the sample to a laboratory and analyzing the samples by GC, GC/MS or other analytical techniques.

TO series EPA Methods are for the determination of VOCs in ambient air. In Method TO-1 and TO-2, a sorbent cartridge containing 1~2 grams of Tenax and carbon molecular sieve is used to adsorb the VOCs from the air sample. Then the

cartridge is transferred to the laboratory. For analysis the cartridge is placed in a heated chamber and purged with an inert gas. The VOCs are thermally desorbed and transferred onto a cold trap. The cold trap refocuses the analyte and injects into GC column to obtain a high resolution chromatogram. In EPA Method OT-14, a whole air sampler such as canister is used for sampling. The canisters are then brought back to the lab for analysis.

Purge-and-trap and headspace methods are used for analysis of volatile organic compounds in drinking water, wastewater and sludge e.g., EPA Method 502.2, 624 and 8240/60. In the headspace analysis, the sample is transferred into a sealed vial and allowed to reach the equilibrium of VOCs between the headspace and sample. Then a small head space sample is withdrawn and analyzed by GC or GC/MS. The headspace method has low sensitivity since only a small volume can be injected into GC. Moreover, the headspace has relative poor accuracy and precision so that it often is used as a screening test. Purge-and-trap methods are the most popular method of VOCs analysis in the United States. In this method, an inert gas is bubbled through a 5 ml water sample contained in a specially-designed purging chamber at ambient temperature or certain temperature. The VOCs in sample are efficiently transferred from aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the VOCs are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the VOCs onto a gas chromatographic column.

Recently Pawliszyn and co-author [2-4] reported solid phase microextraction (SPME) to preconcentrate the VOCs in water samples. In SPME, a stationary phase-coated fused silica fiber is introduced into the water sample or the headspace of sample. Organic analytes adsorb to the phase. Then analytes are desorbed from the fiber to a capillary GC column by the heated chromatographic injection port. No solvents or complicated apparatus is required and the detection

limits for most of VOCs are comparable to purge-and-trap. The SPME methods have not been approved by US EPA and its research on it is still continuing.

These conventional EPA Methods are quite effective in routine environmental analysis. However, there are some disadvantages to face today's environmental law. The major limitation is that the sample has to be sent to the laboratory for analysis so that there is a long delay between sampling and analysis. Thus only delayed information can be obtained. The loss of analytes from the sample and cross contamination between samples may occur during sample handling [5].

1.2 Continuous Analysis

Continuous analysis is the analytical methodology in which a sample stream continuously flows through the analytical system, and which can track analytes in a process all the time. The goal of continuous process analysis is to supply quantitative and qualitative information about a chemical process in real-time or near real-time. Such real-time information can be used not only to monitor and control a process, but also to optimize its efficient use of energy, time, and raw materials. Two factors are largely responsible for the drive toward real-time continuous analysis: regulatory compliance, especially with respect to waste streams, and product quality. Federal legislation mandating that chemical emissions be steadily reduced is also creating increased environmental awareness throughout industry [6]. In the 1980s, chemical methods were applied to real-time process analysis in order to monitor product quality and other properties of the manufacturing process. In the 1990s, increased environmental awareness and corporate responsibility for toxic chemical effluents is driving the need for analytical instrumentation designed for real-time analysis. In the near future, one can even predict, regulatory compliance rather than product quality will become a more significant factor in the use of real-time analysis [6].

According to my interpretation, continuous analysis can be simply identified as: on-line and in-line [7, 8]. In on-line analysis, an automated sampling system is used to extract the sample, condition it, and present it to an analytical instrument for measurement [9]. Thus, the on-line analytical system is permanently linked to the line, and the sample is measured directly in the process line, reaction/blending vessel, or local environment (ambient air monitoring). Measurements are made continuously or at least automatically, without operator intervention. In-line analysis is actually in-situ analysis with the analyzer such as a sensor located inside the process line. This mode of operation is normally limited to sensor devices rather than advanced forms of instrumentation due to constraints of implementation. Although in-line analysis has some advantages, on-line monitoring is much more popular. Most samples need to be conditioned before injecting into instrument because the sample from a process may be dirty or too low in concentration.

Continuous, on-line monitoring offers several advantages over conventional analytical methods. On-line techniques provide a more accurate analysis by overcoming the problems associated with discreet sampling, sample preservation, transportation, storage and laboratory handling samples. Each of these steps may introduce errors such as sample loss and cross contamination etc. In on-line analysis, the emissions can be tracked continuously from an emission source such as industrial stacks, vent and waste water discharge etc. The real-time information can go back to control the process.

Several techniques have been used in on-line monitoring of VOCs in air and water. Infrared spectroscopy (IR) has the ability to provide useful qualitative and quantitative information about the process. Historically, the principal drawbacks of this technique have been the relatively slow acquisition rate for data, its low sensitivity. These two items are no longer an issue now that Fourier transform (FT) instruments allow rapid data acquisition and signal averaging. [10].

Thus, FTIR has been used for continuous analysis. However water vapor which exists in air samples such as stack emissions interferes with the analysis [11, 12] because the water vapor has strong absorption in middle IR. To overcome the water problem, near IR technique has been widely applied to on-line analysis in chemical process control. Usually, we have a few known reactants and products in chemical process and their concentrations are easily tracked using NIR. However, in most environmental applications, it is difficult to determine individual unknown compounds in a complex mixture using an IR technique without any separation.

The mass spectrometer has also been used for continuous monitoring of VOCs in process streams [13]. Direction introduction of sample into mass ionization chamber is a simple configuration of on-line mass spectrometer. However, direct injection has low sensitivity and high detection limits. Membrane introduction mass spectrometer (MIMS) is based on the selective transport of analyte molecules of interest across a semi-permeable membrane into a mass spectrometer [14-16]. The analyte matrices, usually water and air, is excluded from passage through the membrane to varying degrees depending on the membrane material used. This provides a degree of enrichment of the analyte molecules entering the mass spectrometer and allows lower levels of detection than can be obtained using other direct-sampling systems, such as thermospray ionization, which introduces the sample into the mass spectrometer without enrichment. Electron impact (EI) or chemical ionization (CI) spectra may be obtained using MIMS techniques [17, 18]. MIMS has some advantages such as simple, fast response time and low matrix effects. However, there are several limitations of this technique. First of all, the interpretation of mass spectra is very difficult for complex mixtures without any separation. Only a single ion monitoring (SIM) detection mode can be used. Single ion monitoring (SIM), as opposed to full-scan mass spectrometry, may be useful for screening a limited number of analytes; in many cases, the base peaks and fragment ions of small

molecular weight VOCs overlap, causing false positives or high responses for the selected analytes in the SIM mode. Thus, the identification and quantitation of complex, multi-analyte mixtures in streams would be difficult, if not impossible, to achieve without the aid of chromatographic separation [19]. Sometimes a very insensitive spectrum line has to be chosen as quantitative line to avoid the overlap of the spectra. The other limitation of the method is that it is not applicable to larger or more polar compounds [20].

Gas chromatography (GC) is an excellent technique for separating organic compounds in mixtures. There are many commercial packed or capillary columns available for specific applications. Moreover, many commercially available GC detectors are for specific compounds such as ECD for chlorinated compounds, PID for aromatic and conjugation unsaturated compounds, O-FID for oxygenated organics [21] and thermal energy analyzer for nitrosoamine. In conventional gas chromatography a sample is injected once into a GC column by hand or autosampler. However, in many applications, information on VOC concentration variations in a process must be obtained. Thus, it is necessary to take samples frequently and make many repetitive injections with time. Process gas chromatography (PGC) is a GC system which is able to continually monitor compounds of interest in a process. Actually PGC has been used in process stream analysis since 1956 [22]. Unlike spectroscopic techniques in which a sample stream can continuously pass through the detection cell, a pulse injection is needed for PGC system. In a typical PGC system, a series of injections are made intermittently to analyze a process stream. Therefore, a critical component of PGC instrumentation is the sample injection device, which should be able to make automatic, reproducible injections. Multiport sample valves have been used extensively as injection devices for continuous GC analysis [23-27]. A large sample volume is necessary when low concentration samples are encountered. However, a large injection volume is precluded because it requires long injection

time, which generates excessive band broadening. As a result, only a few microliters can be injected and analytes at subparts per million levels can not be effectively determined using a sample valve. Furthermore, the sample valve makes intermittent injections and analyzes the process stream only at the moment when the injection is made.

To obtain real-time or near real-time information on a process, frequent injections have to be made in process GC. However, how frequently injections can be made is limited by the separation time of the GC column. It requires about 20 minute separation time for one sample containing 20 analytes. However, advanced techniques of fast GC [28] and multicapillary columns [29] have shown that separation time can be reduced tremendously. Sack [28] reported separation of ten compounds in 28 seconds using high-speed GC. A revolutionary new GC column, Alltech's Multicapillary, dramatically reduces analysis time without sacrificing sampling loading, or resolution [28]. The multicapillary column combines over 900 liquid-phase coated 40 μm capillaries in a single glass tube, overcoming traditional small diameter capillary column flow, volume and sample capacity limitations. One example of multicapillary column capability is that fourteen compounds can be separated in 2 minutes [29]. These advanced technologies make process GC more attractive for continuous, on-line analysis.

1.3 On-line Microtrap

A microtrap has been used as an injection device for continuous monitoring of VOCs in gas stream [30, 31]. The microtrap is made from a short metallic tube packed with an adsorbent. A typical microtrap has a size of 0.029" o.d. x 0.021" i.d x 6 inch length and is packed with 50 ~ 70 mesh adsorbent. The microtrap has a resistance of about 0.1 Ω/cm. The construction of a microtrap is shown in Figure 2. The ends of the microtrap were filled with glass wool to hold the adsorbents. For a 0.53 mm id microtrap, about 30 mg adsorbent was packed. The microtrap

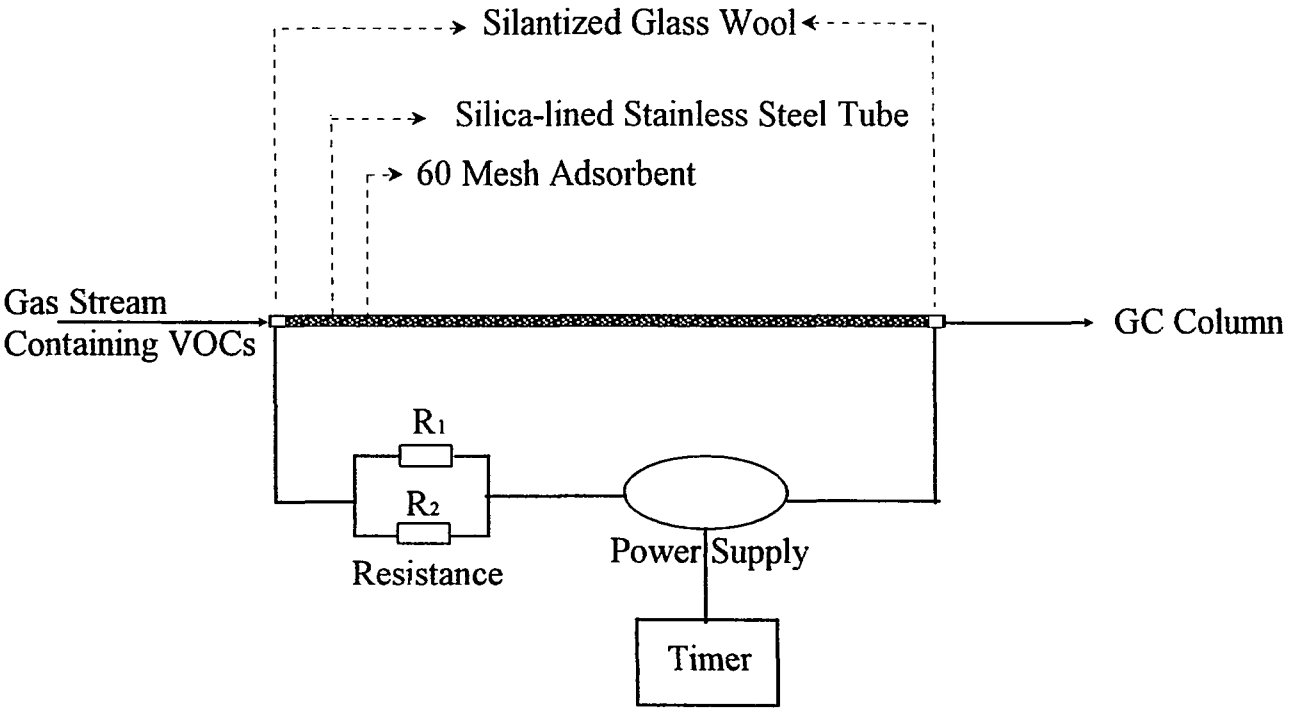


Figure 2 Diagram of an on-line microtrap

was heated by passing current through the wall of the tube. The thin walled, small diameter tube has 1 gram of thermal mass and can be heated and cooled very rapidly.

A Variac (STACO, PA) was used as the power supply, and two or more 5 Ω parallel power resistors (Dale RH-50, Israel) were placed in series with the microtrap to control the current through it. A microprocessor controlled electronic switch (built in-house) or a digital timer (Dimco-Gray Company, Ohio) was used to control the heating time and injection interval. The duration of each pulse was approximately 1.2 second for 0.53 mm i.d. microtrap, and can be longer for a larger size microtrap. The voltage of power supply was set at 30 volt. It is difficult to measure the exact heating rate and the temperature accurately by using a conventional temperature measuring devices. However, a measurement using a thermocouple showed that a temperature as high as 300 °C was reached in 1 to 2 seconds [123].

The microtrap is placed in front of GC column instead of a conventional injection port and referred to as an on-line microtrap (OLMT). This OLMT GC system is shown Figure 3. The sample stream continuously flows through the OLMT and into the GC column. The VOCs in the sample are trapped by the adsorbent in the microtrap. Then the VOCs are released and injected into the column by rapid electrical heating combined with purge gas flow. Because the microtrap has a low thermal mass, it can be heated very rapidly. The fast desorption generates a "concentration pulse" which serves as an injection. Continuous monitoring is done by heating the microtrap at fixed interval of time and corresponding to each heat pulse a chromatogram is obtained. If necessary, the OLMT pulses can be made every few seconds and the minimum interval between consecutive pulses depends upon the time required for chromatographic separation. Since the microtrap accumulates the analytes during the interval between two pulses, it is an injection device as well as a preconcentrator. The

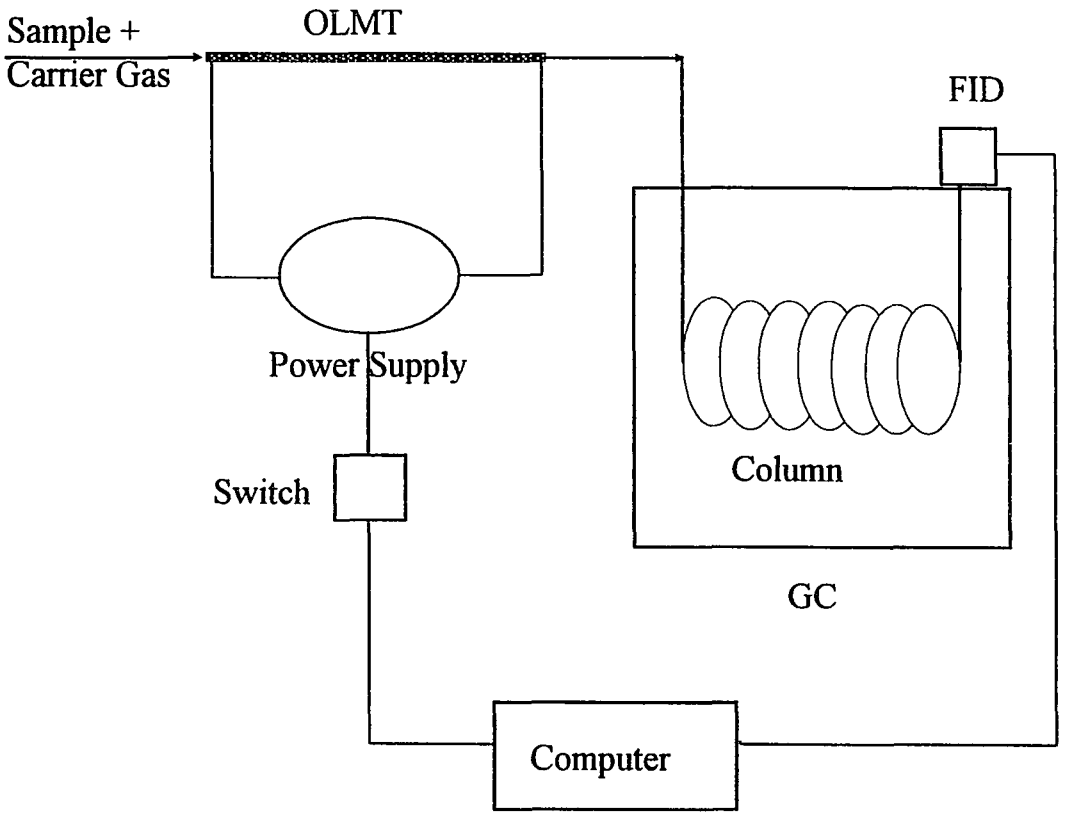


Figure 3 Continuous monitoring of VOCs using OLMT.

preconcentration capability of the OLMT makes it be a very sensitive device. Figure 4 presents a typical chromatogram of continuously monitored VOCs at sub parts per billion levels [30]. However, this analytical configuration has some limitations in practical applications. The air sample was directly introduced into GC column and detector through the OLMT. Actually, the matrix gas of sample served as a part or all of carrier gas. The undesirable components in sample stream such as oxygen and moisture may deteriorate the stationary phase of column. In this OLMT system, the GC system was never isolated from the sample stream and this can cause some practical difficulties. For instance, it is common practice to use one GC to analyze several different process streams by switching between several lines. Line switching is not easy with the OLMT [31]. Moreover, a pressurized sample was needed in this system to introduce the sample into the OLMT analytical system. But the presence of a pressurized sample is not common and a pressurizing pump may cause large dead volume and contamination. On the other hand, the analytes, which broke through from the OLMT, went directly to the detector and contributed to the baseline of chromatogram. Thus an unusual chromatogram would be obtained which might cause problems in the integration of these peaks [32].

A sequential valve microtrap system (SVM) which combines a sample and a microtrap has been reported recently [31]. Figure 5 shows a diagram of sequential valve microtrap GC system. The sample stream continuously flowed through a sample valve with a large loop (or multiple injections by small loop). Then a large volume sample was injected into the microtrap by a sample valve. The microtrap trapped the analytes from the large injection volume. Finally a microtrap pulse was made which served as an injection for GC column. If the valve alone were used to make a large volume injection, poor chromatographic separation would be obtained. The SVM can make a large volume injection and still show a good chromatographic resolution since the microtrap pulse is sharp

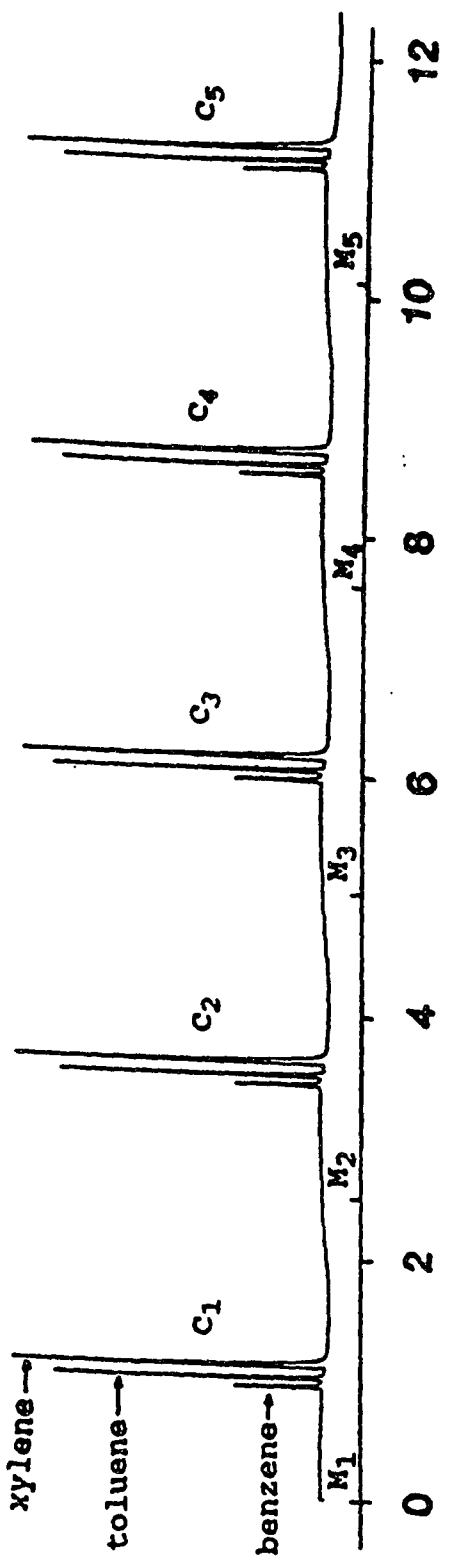


Figure 4 Continuous on-line analysis. A 6.5 cm long fused silica microtrap was used and ppb, levels of benzene, toluene and xylene were used as the samples.

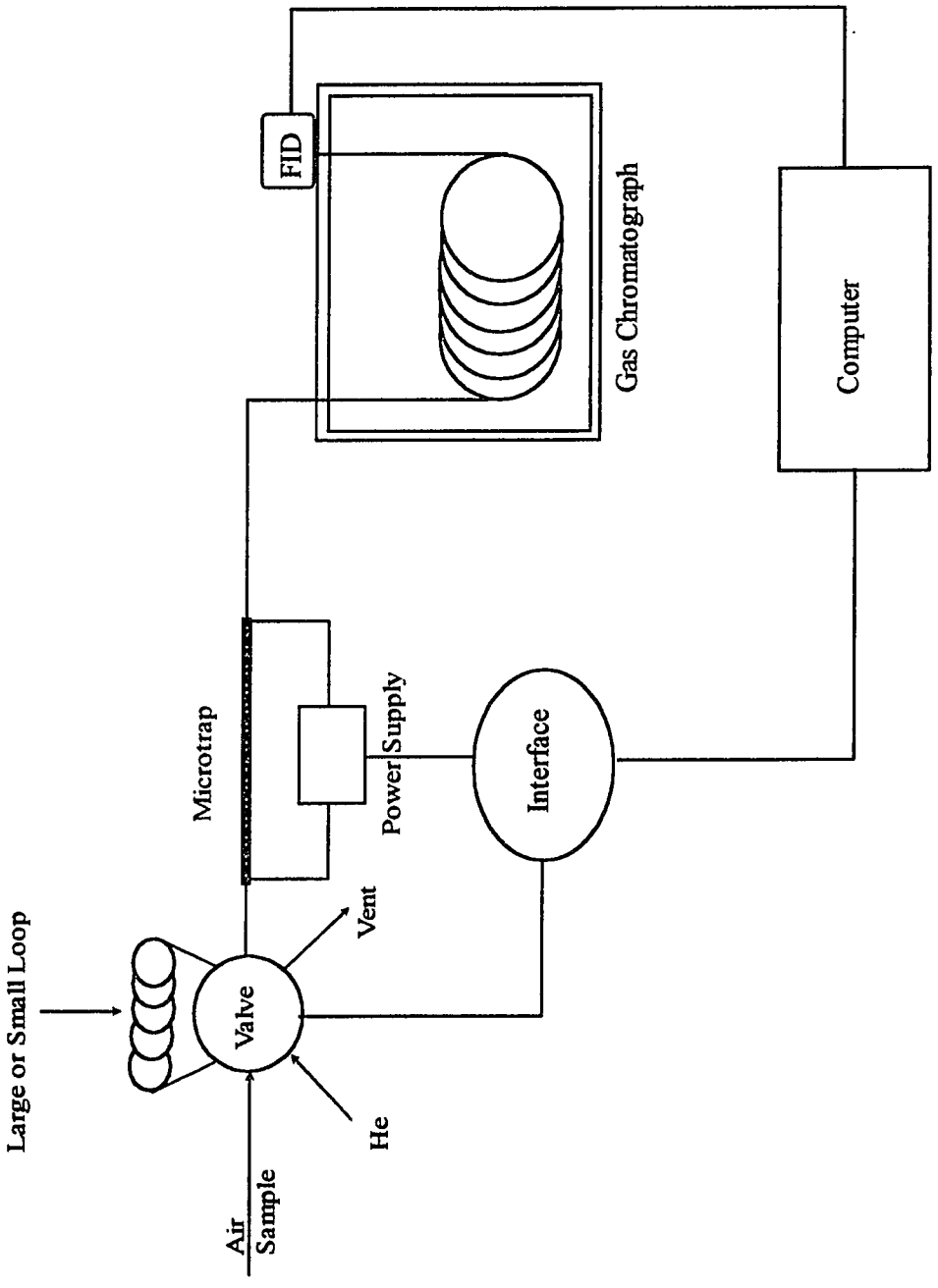


Figure 5 Sequential valve microtrap GC system

enough. The system can be operated in two different ways. Either a small sample loop is used to make a series of injections from the valve prior to a microtrap pulse, or, a large sample loop makes a single injection followed by a microtrap pulse. In either case a large amount of sample is analyzed which increases the sensitivity and lowers the detection limits. The SVM also isolates the sample stream from GC system. But there is still a large volume of sample matrix which passes into GC column, which may cause problems. Since a sample valve is used to take the sample, the information of two injections in process can not be obtained. Moreover, the SVM system has low sensitivity compared to OLMT in a fixed injection cycle time.

1.3.1 Theory of Trapping Efficiency of The Microtrap

The principle of an on-line microtrap is similar to that of thermal desorption modulators (TDM) [30, 32, 58, 60]. Both adsorption and desorption process play important roles in the on-line trapping \desorption involved in the continuous monitoring. The effect of capacity factor in thermal desorption modulators and the microtrap are described in the literature [32, 60].

Trapping or modulation efficiency of the microtrap is defined as the fraction of the sample retained by the microtrap and total incoming sample before an injection is made:

$$\text{Trapping efficiency (T)} = \frac{\text{sample amount retained}}{\text{sample amount entering microtrap}} = \frac{t_b C_s}{t_i C_t} = \frac{t_b C_s}{t_i (C_s + C_m)} \qquad (1.1)$$

where, C_s is the amount of sample trapped per unit time in stationary phase (adsorbents); C_m is the amount of sample in the mobile phase, C_t is the sample

amount per unit time flowing into the microtrap, t_b is the breakthrough time and t_i is the injection interval between two pulse injections of the microtrap.

The capacity factor k is defined as the partition ratio of the analyte mass in the stationary phase to the analyte mass in the mobile phase. Thus, the capacity factor k equals the ratio of C_s to C_m. Thus the above equation reduces to:

$$T = (t_b/t_i)k/(k+1) \quad (1.2)$$

If the injections are made very frequently such that $t_b \geq t_i$, the microtrap accumulates sample only during the time t_i and the above equation becomes:

$$T = k/(k+1) \quad (1.3)$$

In this case, the trapping efficiency depends only upon capacity factor. If the injection interval $t_i > t_b$, the trapping efficiency is given by equation (1.2) and is inversely proportional to t_i.

1.4 Theory of A Sorbent Trap

The adsorbent methodology using a sorbent trap packed with adsorbents has been becoming one of most common method for sampling and preconcentrating VOCs in air. When sampling, air sample containing VOCs continuously flows through a sorbent trap and the VOCs can be trapped. However the maximum permissible sample volume for quantitative trapping of a compound by a sorbent trap is related to the breakthrough volume. The term, breakthrough volume (V_b), can be defined in as the total sample volume passing through the trap with better than 99% adsorption efficiency [33]. The retention volume (V_R) is defined here as the gas volume which pass through the trap before the point at which a single injection of vapor reaches its maximum concentration in the effluent from the trap. Therefore, the breakthrough volume is definitely smaller than the retention volume. Figure 6 explains the concept of breakthrough and retention volume in single injection method. The breakthrough time (t_b) is defined as the time required for an analyte to break through the trap, with 99% adsorption efficiency. Thus the breakthrough

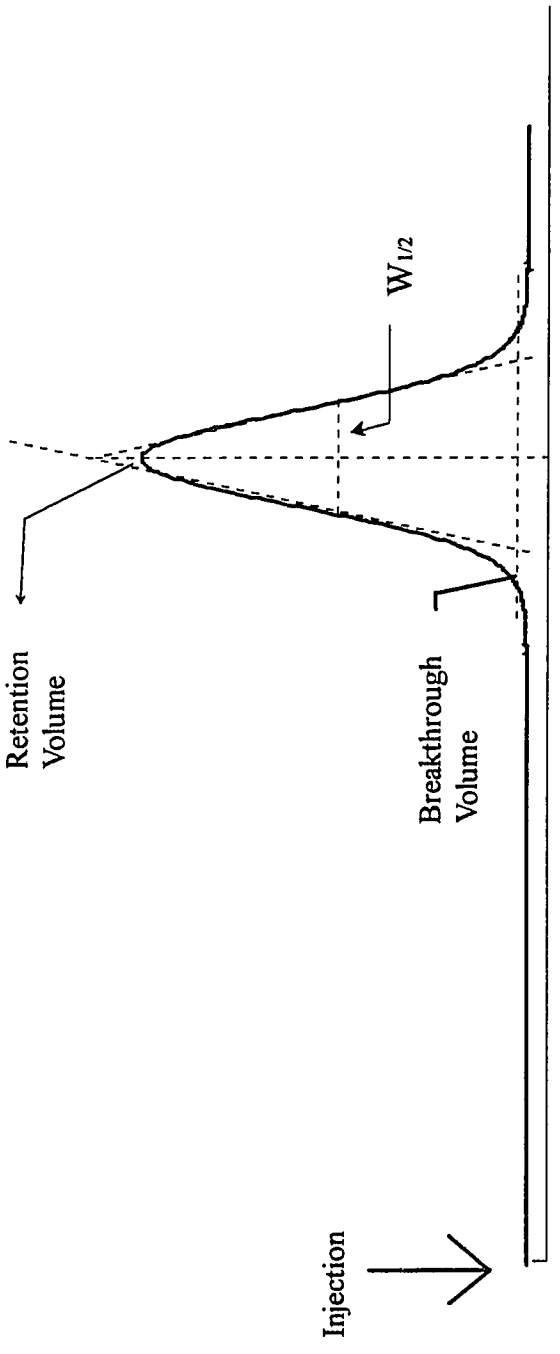


Figure 6 A typical GC chromatogram using single injection.

time can be calculated from the breakthrough volume (V_b) and the sampling flowrate:

$$t_b = \frac{V_b}{F} \tag{1.4}$$

Here, V_b is the breakthrough volume (ml), and F is the volumetric flowrate of the gas sample through the trap (ml/min).

Similarly, the retention time (t_R) is defined as the time of the maximum concentration in the effluent from a single injection of vapor emerging from the trap. The retention time (t_R) can be calculated as follows:

$$t_R = \frac{V_R}{F} \tag{1.5}$$

Here, V_R is the retention volume (ml), and F is the volumetric flowrate of the gas sample through the trap (ml/min).

There are two methods to measure the breakthrough volume of analytes in a sorbent trap [34, 35]. They are a frontal analysis and GC injection method. In frontal analysis, a gas stream containing analyte continuously flows through a trap and the effluent is monitored by flame ionization detector (FID). Figure 7 shows a typical chromatogram of frontal analysis. In GC injection method, the trap is connected to the injection and detection ports of a conventional GC with FID. A conventional injection is made and the effluent is monitored by FID. Table 1 lists some data of breakthrough volume by the frontal analysis and GC injection method. Very good agreement is observed for the light compounds, but total disagreement for the heavier compounds [34].

In previous studies [30, 58, 60], two methods have been used to measure the breakthrough time in the microtrap. First method was called the t- method [60]. In this method, the duration of the negative peaks were measured by first making a series of pulses to remove all organics from the microtrap, while the sample continues to flow through the trap. Then a pulse is made to desorb the retained substances. First a desorption peak is seen. This is followed by a negative peak as

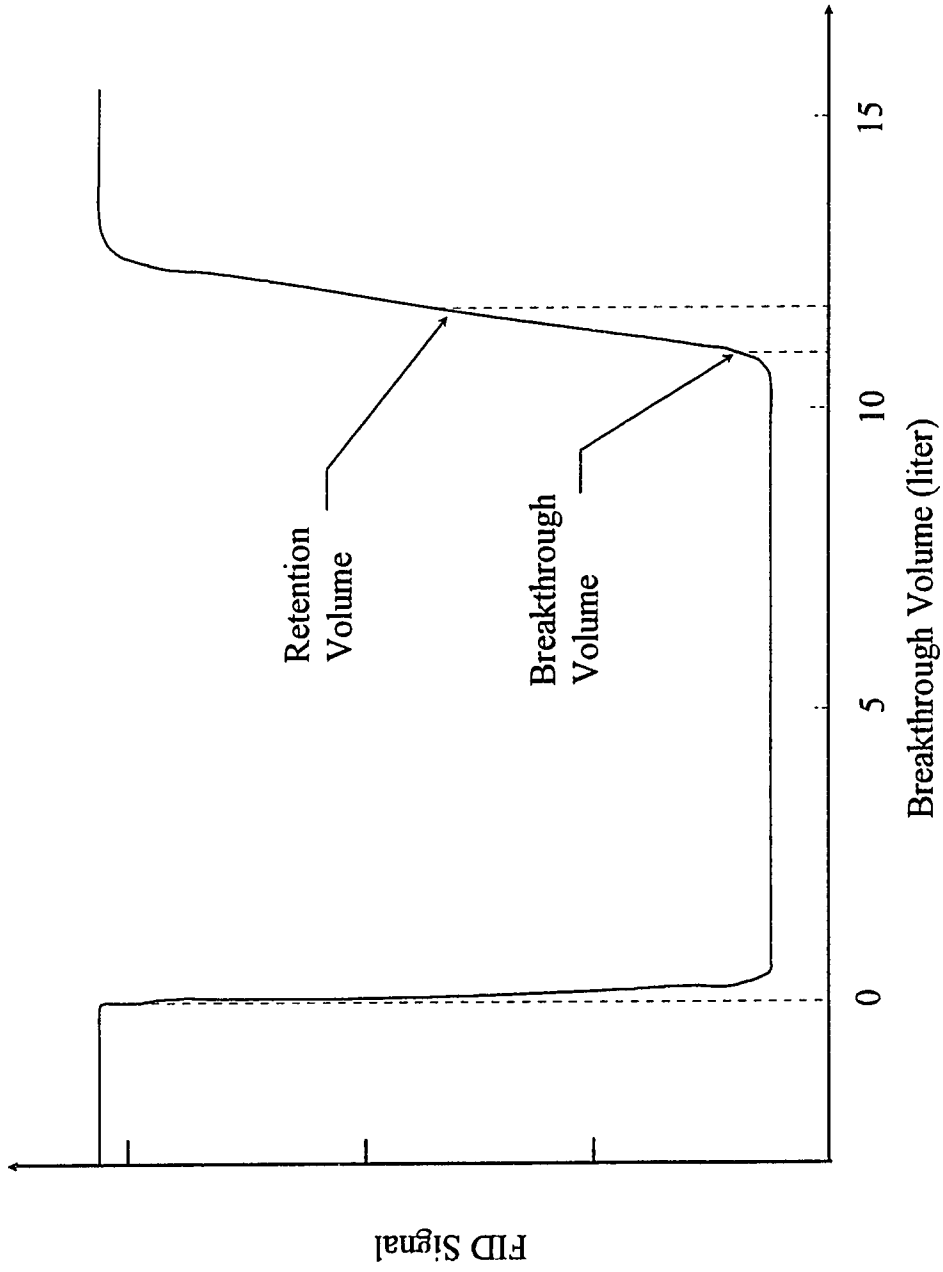


Figure 7 A typical chromatogram of frontal analysis.

shown in Figure 8. The duration of the negative peak has been assumed to be the breakthrough time. The other method which has been used to measure the breakthrough time was the pulse interval method [60]. In pulse interval method, the sample stream continuously flowed through the microtrap. For each pulse interval, an electrical pulse was applied to release the analyte from the microtrap. A FID detector monitored the effluent. The peak area was recorded for each pulse. A plot of peak area against pulse interval was made. The time at the inflexion of the curve was the breakthrough time. Figure 9 is a typical curve of pulse interval method.

The breakthrough volume varies with parameters such as sampling flow rate and operating temperature.

Table 1 Breakthrough Volume * at 20 °C [34]

Compounds	Breakthrough Volume (liter)	
	GC Injection Method (extrap. at 20 °C)	Frontal Analysis (extrap. at 1 ppm)
CH_2Cl_2	0.29 ± 0.02	0.18 ± 0.02
iso-C_4	0.40 ± 0.02	0.4 ± 0.02
$CHCl_3$	3.2 ± 0.30	2.9 ± 0.30
Diethyl ether	5.0 ± 0.50	4.4 ± 0.5
n-C_5	8.7 ± 0.50	8.0 ± 0.5
n-C_6	300 ± 30	20.5 ± 2.0
n-C_7	5000 ± 500	76.0 ± 4.0

* A Carbopak B (20-40 mesh) (Supelco) glass column (50 x 0.4 cm i.d.)

1.4.1 The Sampling Flow Rate Effect

The characteristics of a sorbent trap are similar to these of a GC column. Thus the theory describing a GC column can be applied to a sorbent trap. According to the

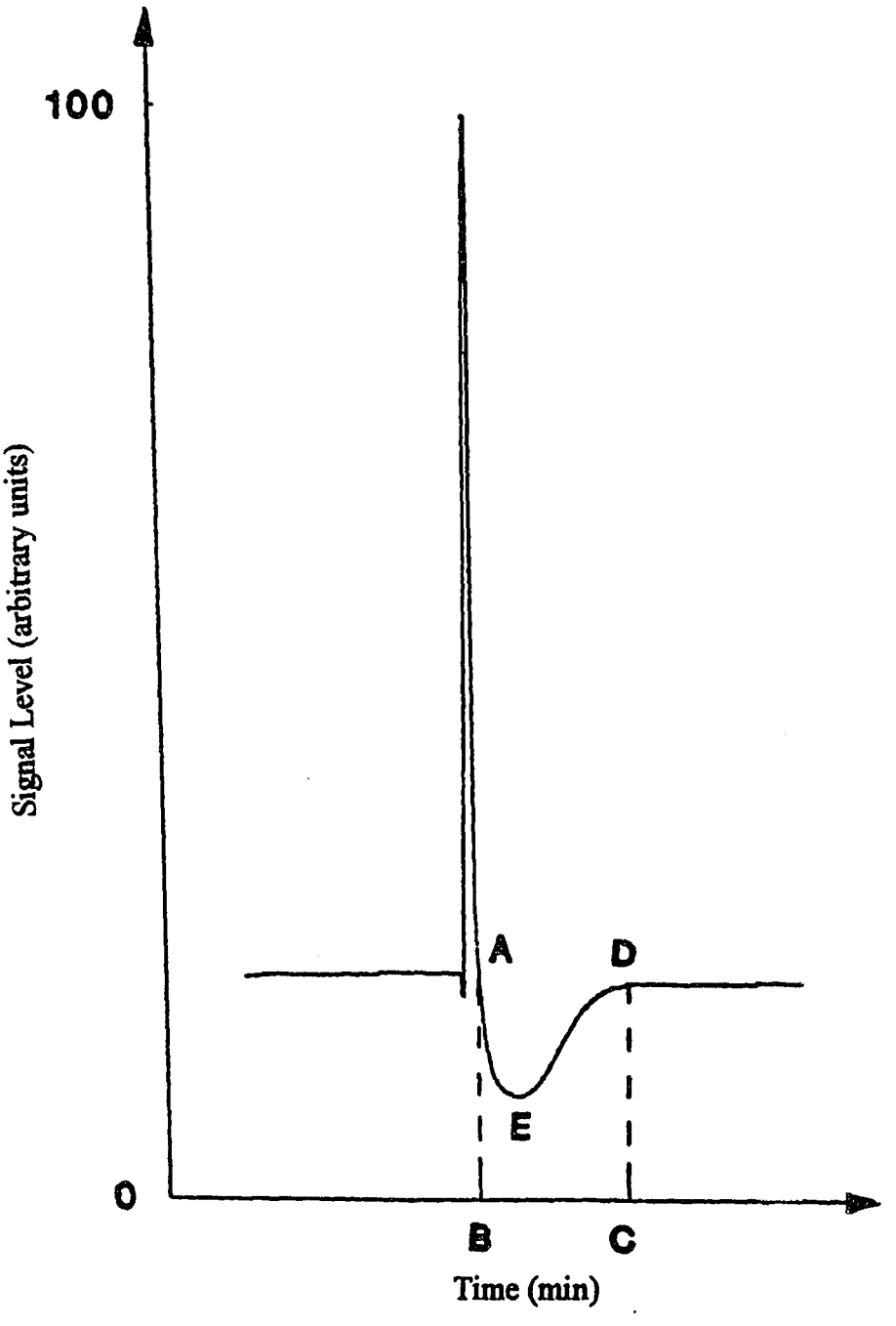


Figure 8 A typical chromatogram of a microtrap [60]

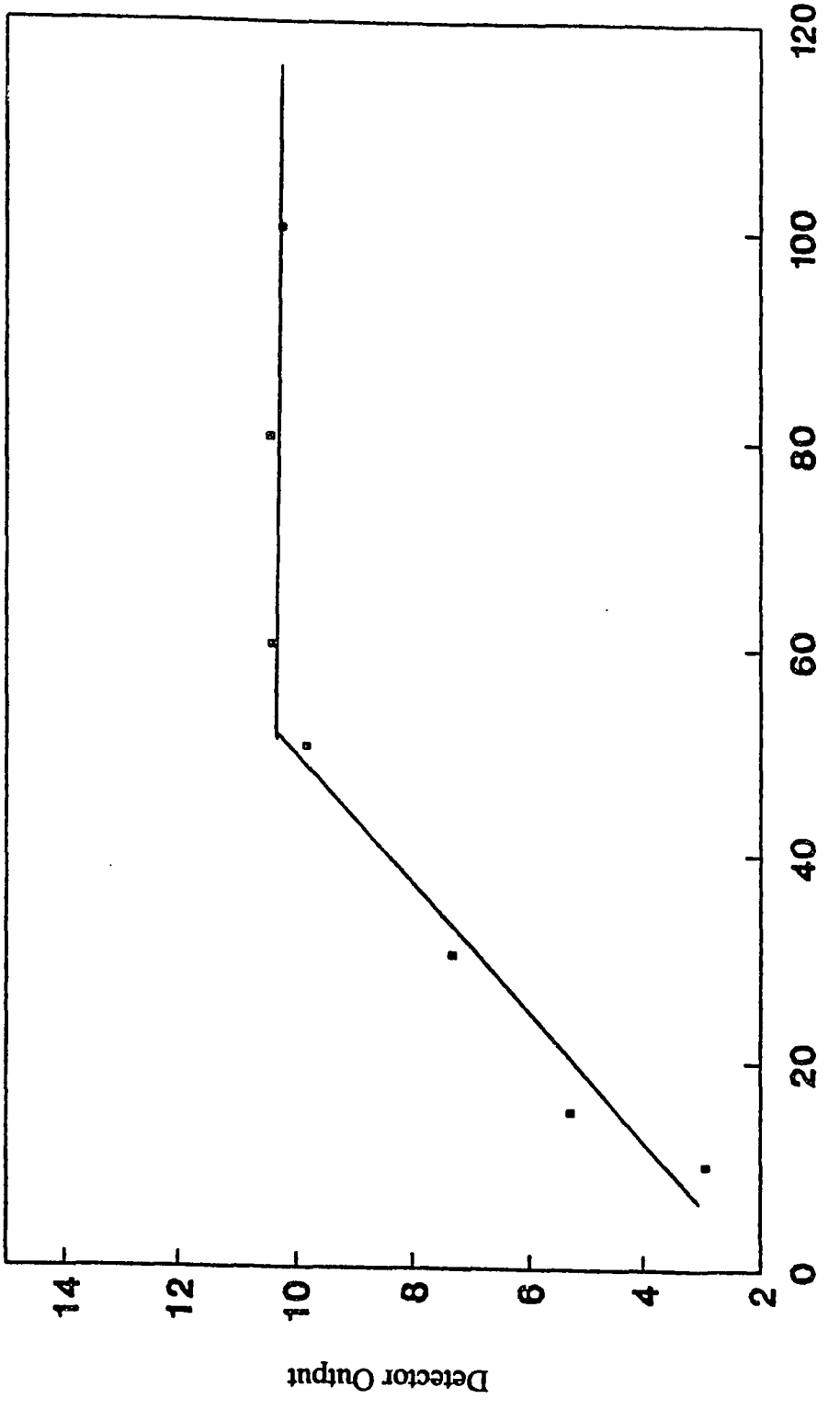


Figure 9 Response of Carbotrap C microtrap as a function of pulse interval

Van Deemter equation [36], the flow rate would affect the theoretical plate number of the trap. The theoretical plate number can be measured by injecting a known amount of a analyte into the trap at three different temperatures. The effluent at the end of the trap was monitored and the typical chromatogram is presented in Figure 6. The retention time (t_R) and peak width ($W_{1/2}$) can be obtained from the GC chromatogram. Thus, the theoretical plate number (N) of the trap can be calculated:

$$N = 5.54\left(\frac{t_R}{W_{1/2}}\right)^2 \qquad (1.6)$$

Here N is the theoretical plate number of the trap. t_R is the retention time (min) and $W_{1/2}$ is peak width at half peak (min).

The sampling flowrate can affect the plate number of the trap. A typical relationship between the plate number and linear velocity is presented in Figure 10. Thus the sampling flow rate does significantly affect the theoretical plate number of the trap. Theoretically, although the plate number varies the retention volume should remain constant when the sampling flowrate increases. The higher theoretical plate number, the higher efficiency the column (or trap) has. Therefore, the sampling flowrate could affect the breakthrough volume. Cropper et al [37] developed a mathematical model to predict how the theoretical plate number of a trap influences the sampling efficiency.

In this model, it was assumed that a distribution of analytes in the trap is approximately a Gaussian type curve. The sampling volume (V_s) is defined as the total gas sample volume of which the sample passes through the trap during the sampling. Consider a sampling volume V_s equal to the retention volume (V_R), and let both equal 100 arbitrary units, which can be labeled with i from 1 to 100. It is clear that the compound will not be retained quantitatively on the trap, since the peak maximum corresponding to the first unit will have reached the end of the trap. Thus the compound in this first unit will be only 50% retained on the trap.

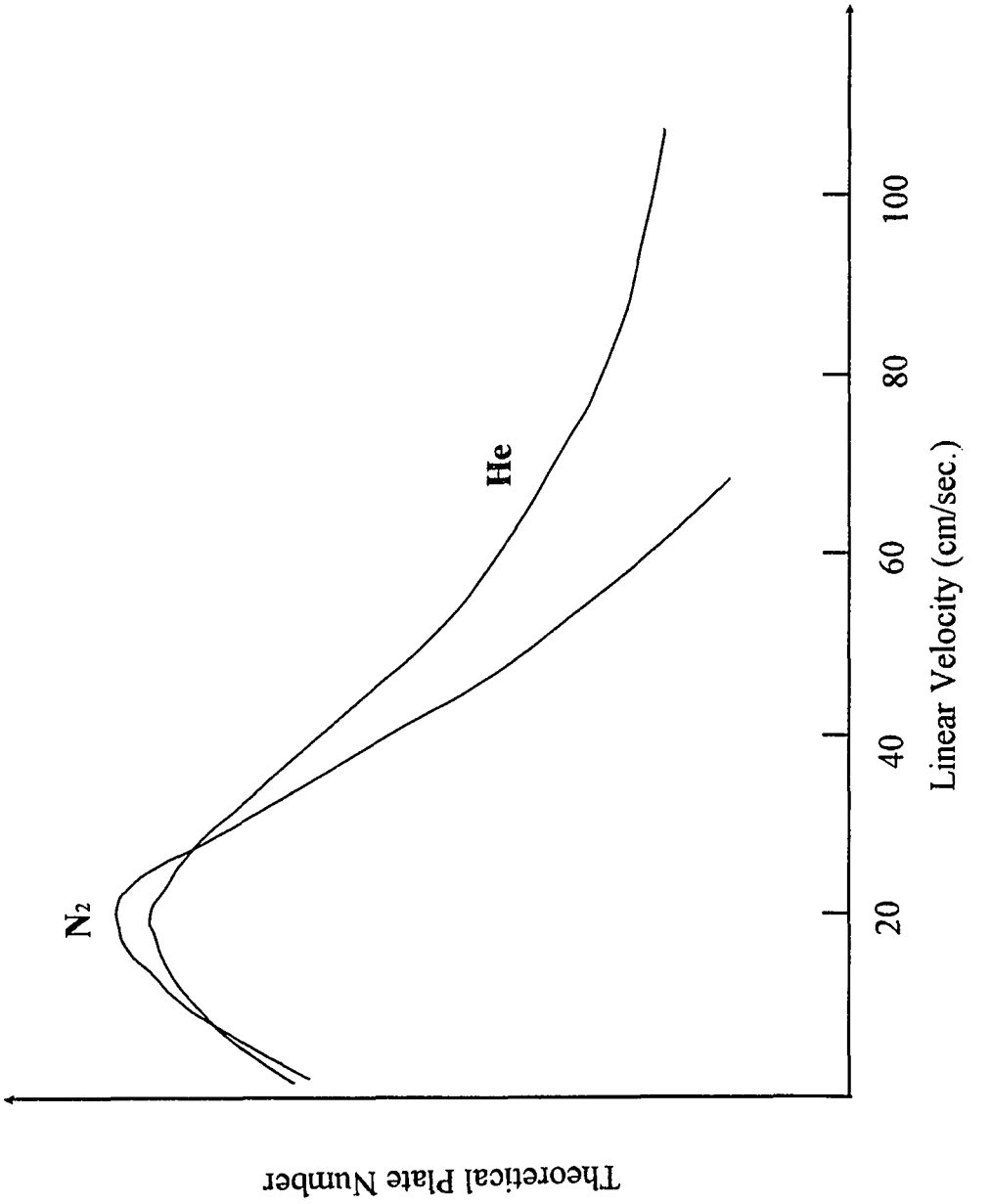


Figure 10 Van Deemter curve

This percentage will, however, increase for the successive units until a unit is reached, corresponding to the breakthrough volume. This can be defined as sampling volume at 100 % trapping efficiency; all one hundred succeeding units will be also 100% retained. The distribution of each unit will approximate to a Gaussian type towards the outlet end of the trap.

The standard deviation of Gaussian curve is defined as $\sigma = V_R / \sqrt{N}$ [37, 124], N is the number of theoretical plates in the trap. Therefore, the bigger the number of theoretical plates, the smaller the standard deviation and the sharper the elution profile of analyte in the trap. Figure 11 shows the elution profile at different deviations. Consider the distribution of the i_{th} unit of sample volume; the extent to which this is not retained on the trap is given by that fraction of the area under the curve of the probability integral outside the bounds of the trap (See Figure 12). In Figure 12, the ABC area is 0.5 and the ABtt' area can be calculated as follows:

$$\text{Area of ABtt'} = 1/\sqrt{2\pi}\int_0^t \exp(-t^2/2)dt \qquad (1.7)$$

Thus, the area of tt'C which stands for unretained portion can be calculated as follows:

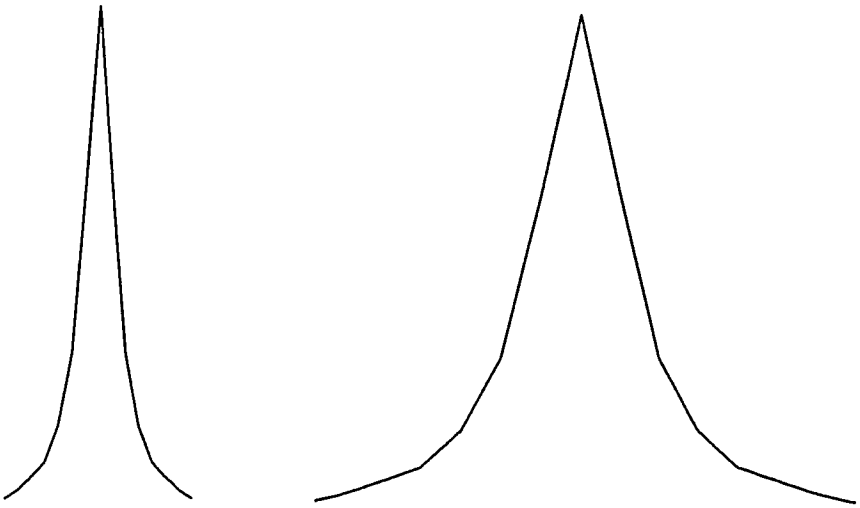
$$0.5 - 1/\sqrt{2\pi}\int_0^t \exp(-t^2/2)dt \qquad (1.8)$$

The percentage of the total sample not retained on the trap is therefore:

$$i_{lost} = \sum_{i=0}^{i=100}\left[0.5 - 1/\sqrt{2\pi}\int_0^t \exp(-t^2/2)dt\right] \qquad (1.9)$$

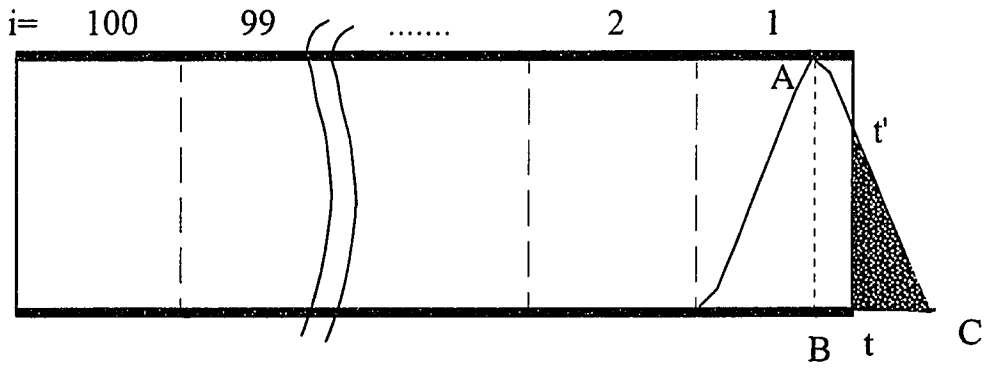
where t is the ordinate of the normal curve of error and $t = i/\sigma$ [37].

The sampling efficiency (%) = 100 - i_{lost}. Thus when a retention volume is taken as a sampling volume, the sampling efficiency will increase with the increase of the number of theoretical plate of the trap.



N bigger, σ small, peak sharp N small, σ bigger, peak broad

Figure 11 Elution profiles of analyte in the trap



$$tt'C \text{ area} = 0.5 - 1/\sqrt{2\pi}\int_0^t \exp(-t^2/2)dt$$

Figure 12 Explanatory diagram of Cropper's model

1.4.2 The Effect of Temperature on Breakthrough Volume

Temperature has only a small effect on theoretical plates and peak asymmetry [38]. It has a much more serious effect on retention volume and breakthrough volume. When the GC injection method is used to determine the retention volume and breakthrough volume, the trap is equivalent to a short GC column. The retention time (t_R) depends upon its capacity factor [30]:

$$t_R = (k + 1)L/\mu \tag{1.10}$$

where k is capacity factor; L is the length of the trap and μ is the linear velocity of carrier gas. Since the retention volume (V_R) is the product of t_R and the volume flowrate, equation (1.8) can be changed :

$$V_R = AL\,(k+1) \tag{1.11}$$

where A is the cross section area of the trap. For a given adsorbent and trap, the capacity factor for a certain analyte is a function of temperature. An empirical equation of the following form has been suggested [39]:

$$k = k_0 \exp.(-\Delta H/RT) \tag{1.12}$$

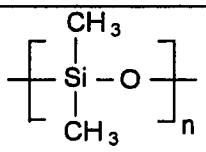
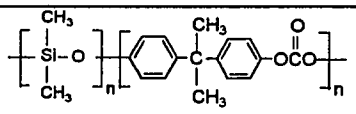
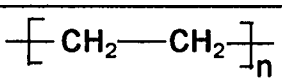
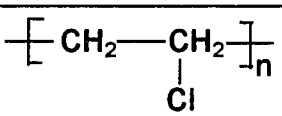
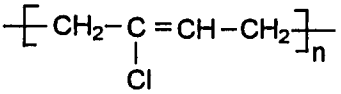
here k_0 is the capacity factor at reference temperature; ΔH is an absorption energy of the analyte in the adsorbent; R is a constant and T is the temperature of trap. Therefore as the temperature increases the capacity factor decreases so that breakthrough volume decreases.

1.5 Membrane Extraction of VOCs

In a continuous, on-line analysis, an automated sampling system is designed to extract the sample, condition it, and present it to an analytical instrument for measurement. In EPA Method 504.2 and 624, the purge-and-trap technique is used to extract the VOCs from water sample. This process requires an average of 20 to 45 minutes for each sample, which is not enough fast response for most environmental chemists and process engineers [12]. Water interference also is a problem in the purge-and-trap technique [40].

The use of membrane to extract the VOCs selectively from water is one of the most exciting and significant emerging technologies in recent years [41-43]. There are two types of membrane that can be used for separation: "porous" and "nonporous" membrane. The porous membrane separates the compounds on the basis of their molecular size by diffusion through small pores [41]. This membrane has been widely used in gas separation and hollow fiber liquid membrane separation [42, 43]. A nonporous membrane has no holes or pores in the common sense. The separation mechanism of this nonporus membrane is a combination of solubility and molecular diffusion. The selective permeation of the analytes through the membrane relies on the solubility and diffusion coefficient of the analytes on the membrane. Table 2 lists some commercial available membranes for VOCs extraction. Silicone rubber from Dow Corning has proven to be the best nonporous membrane for extraction of most of VOCs from water [44, 45].

Table 2. Candidate Polymer Membranes for VOCs Permeation

Polymer	Chemical Formula	Supplier
Polydimethylsiloxane		Dow Corning
Silicone polycarbonate (GE-MEM-213)		General Electrical
Polyethylene		Dow Corning
Polyvinyl chloride		Goodrich
Neoprene (chloroprene)		DuPont

Membranes are available in a variety of forms and shapes. Flat sheets are often used, especially for dialysis, and can be manufactured in long rolls and then assembled into plate-and-frame or spiral wound configurations. The spiral-wound approach provides a higher area/volume ratio than the plate-and-frame. Hollow fiber membranes are small tubing with outer diameters ranging from as little as 50 microns to over 500 microns. The hollow fiber has a larger surface area per volume resulting in a more efficient extraction and also provides even high higher packing densities. Thus it is a more useful geometry for analytical applications [45].

Many applications of on-line membrane introduction mass spectrometry (MIMS) [14-16] have been described for continuous monitoring of VOCs in water streams. As mentioned above, the interpretation of MS spectra from MIMS is difficult for real samples which may contain a mixture of organics because no chromatographic separation is done. Several studies have been published using on-line membrane module and sample valve as interface in process gas chromatography [47, 48]. Since the sample valve can not hold/concentrate the analytes from the membrane module, this system may lose the enhancement effect of the membrane. Another approach [49] used a cryogenic technique to preconcentrate/refocus the analyte from the membrane module in the front of column. But this cool/heat process is very slow and the injection frequency is limited.

1.6 Theory of Membrane Extraction of VOCs

In general, the membrane processes are composed of the feed stream (sample), the reject stream (waste or vent), and the permeate stream (sample extract). The permeate stream is enriched in the analytes due to the selective permeation properties of the membrane. The permeation of a substance through a nonporous membrane can be divided into three broad steps. First, when the aqueous sample

containing the analyte is brought into contact with the membrane, some of the analyte is dissolved into the surface of the membrane by partition coefficient between membrane and water sample. Secondly, the analyte which is dissolved in the membrane selectively diffuses across the membrane wall to the membrane/extractant interface. In the third step, the diffused analyte on other side is removed from the membrane by the extractant/stripping gas.

When a nonporus hollow fiber membrane is used to extract the analytes from a water sample, the diffusion through the membrane is assumed to be the rate-determining process, if the water sample and stripping gas have high enough flow rate. The sensitivity of a membrane separation technique is determined by the steady-state permeation response, while the non-steady-state permeation characteristics of the analyte in the membrane determine the response time. The term permeation is therefore used to describe the overall mass transport of gas across the membrane, whereas the term diffusion refers only to the movement of the gas inside the membrane matrix [50].

1.6.1 Fick's Law

The rate of permeation, F, is defined as the amount of penetrant passing during unit time through a surface of unit area. Consider a unit area of film L cm thick exposed to sample on one side and a low pressure stripping gas on the other side.

In the steady state of flow, the rate of permeation is directly proportional to the concentration gradient as expressed by Fick's first law of diffusion:

$$F = -D\,(\partial C/\partial X) \tag{1.13}$$

Where D is defined as the diffusion coefficient; C is the concentration of the penetrant in the membrane at a position coordinate X. Assuming D to be constant, for a hollow fiber membrane, Fick's first law gives:

$$F = 2\pi LD(C_1-C_2)/\ln(r_o/r_i) \tag{1.14}$$

Where L is the length of the hollow fiber; C_1 and C_2 are the concentration of the substance in the high- and low-pressure surfaces of membrane, respectively; and r_0 and r_i are the outer and inner radii of the hollow fiber, respectively. If the low-pressure side of the membrane is swept with a stripping gas, C_2 becomes very small relative to C_1 and can be ignored. The concentration C_1 is established by the partitioning process and is directly proportional to the concentration in the sample C_0. Thus $C_1 = KC_0$, where K is partition coefficient of the analyte between membrane and aqueous solution. Equation (1.12) then becomes to

$$F = 2\pi LDKC_0/ln(r_0/r_i) \tag{1.15}$$

In non-steady state, the permeation is governed by Fick's second law:

$$\frac{\partial C}{\partial t} = -D\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{1.16}$$

where $\partial C/\partial t$ is the rate of change in concentration with time, t, at a position coordinate X. The mathematical solution for diffusion through a membrane of thickness L following a step change in sample concentration is [51].

$$F_t = F_{ss}\{1+[2\sum(-1)^n \exp(-(n\pi/L)^2 Dt)]\} \tag{1.17}$$

where F_t is the rate of permeation at the time, t; F_{ss} is the rate of permeation at steady state and n is an integer from 1 to infinite.

1.6.2 Effect of Temperature

The mechanism of permeation in nonporous membrane is a combined sorption and diffusion process. The permeability constant P is defined as the product of diffusion coefficient (D) and solubility coefficient (S) [52].

$$P \equiv DS \tag{1.18}$$

Both the diffusion and the solubility coefficients for nonporous membrane systems are usually exponential functions of temperature and can be expressed by the following Arrhenius-type relationship:

$$D = D_0 \exp(-E_d/RT) \tag{1.19}$$

and

$$S = S_0 \exp(\Delta H_s/RT) \tag{1.20}$$

where E_d is the apparent activation energy for diffusion process and ΔH_s is the apparent heat of solution; D_0 and S_0 are constants; R is the universal gas constant and T is the absolute temperature.

The temperature dependence of permeability over small ranges of temperature can be represented by Arrhenius-type relations:

$$P = P_0 \exp(-E_p/RT) \tag{1.21}$$

where E_p is the apparent activation energy for the over-all permeation and P_0 is a constant.

From the definition of P as the product DS, it follows that

$$E_p = E_d + \Delta H_s \tag{1.22}$$

and

$$P_0 = D_0 S_0 \tag{1.23}$$

The sign of E_p in Equation (1.20) depends on E_d and ΔH_s. E_d is always a positive quantity and the sign of ΔH_s may vary with the different permeate.

CHAPTER 2

RESEARCH OBJECTIVES

The objectives of this research are to characterize the microtrap as an on-line preconcentrator as well as an injection device for continuous monitoring of volatile organic compounds (VOCs); to develop a microtrap based gas chromatographic system for continuous monitoring of VOCs in air stream; to establish an on-line membrane extraction-microtrap GC system for continuous monitoring of VOCs in water stream; to investigate continuous monitoring system of nonmethane organic carbon in air using the microtrap based NMOC analyzer, and to evaluate a minitrap-canister system for VOC analysis in ambient air.

CHAPTER 3

CHARACTERISTICS OF MICROTRAP AS AN ON-LINE PRECONCENTRATOR AND INJECTION DEVICE FOR CONTINUOUS MONITORING GC SYSTEM

3.1 Background

A multi-port sample valve is one of most commonly used injection device for continuous monitoring chromatographic system. However, the sample valve is not suitable to trace analysis since only a small amount of sample can be injected into GC column. Sorbent traps and cryogenic traps are commonly used as preconcentrators of VOCs in air analysis [53, 51]. A common sorbent trap is 11.5 cm long x 6 mm o.d. x 4 mm i.d. and is able to preconcentrate the VOCs at ambient temperature. But it requires several minutes to release the trapped VOCs into GC column using thermal desorption. Thus a focusing trap is need to keep high resolution for GC. The cryogenic trap can be heated very fast and can be used as an on-line preconcentrator and injection device. But the operation of a cryogenic trap is expensive and inconvenient for continuous monitoring since it is cooled by liquid nitrogen. Coexisting moisture in sample will cause the practical problems such as blocking the trap and limiting sample volume, as the water vapor is condensed and frozen.

Thermal desorption modulator (TDM) has been developed as a modulation device for sample introduction in chromatography [55, 56, 57]. The thermal desorption modulator is a short segment of fused silica capillary column placed at the front of analytical column. The modulator is coated externally with an electrically conductive paint so that it can be heated by a pulse of electric current. When the air sample is continuously passed through the modulator, a small part of sample is retained in the stationary phase of modulator. Then a heating pulse is applied to make an injection. For each injection a positive peak and negative peak can be seen in detector output. This is unlike a conventional chromatogram and

looks like the derivative of a chromatogram. Some of the problems associated with the modulator are low sensitivity, low modulation efficiency, inability to modulate very volatile components and the derivative peak shape [58].

In principle, the microtrap is similar to the TDM. An on-line microtrap (OLMT) is a small diameter tube packed with an adsorbent(s). The typical diameter of microtrap is 0.53 mm i.d. x 0.73 mm o.d. When a sample stream continuously flowed through the OLMT the VOCs can be trapped selectively. Then a heat pulse is applied to desorb the trapped analytes into GC system. The OLMT can be heated very quickly, since it has relatively small thermal mass. Thus the microtrap can be used as an on-line preconcentrator and injection device. However, the typical packed amount of adsorbent in a microtrap is 30 to 60 mg. Thus the microtrap only retains the analytes for a short period of time.

The on-line microtrap is quite different from the thermal desorption modulator (TDM). The main purpose of TDM is the modulation of output signal since the microtrap is designed for an on-line preconcentrator and injection device. The common TDM has very small capacity factor so that it is impossible to trap the analytes quantitatively.

In this research, the characteristics of the microtrap were investigated and the trapping and desorption efficiency of microtraps was studied.

3.2 Experimental

3.2.1 Microtrap

The microtraps used in the study were made of various diameters stainless steel tubing, some of which were lined with silica. The microtrap was typically 6 inch long, and the diameters were 0.53 mm i.d. x 0.74 mm o.d., 0.74 mm i.d. x 0.86 mm o.d., 2 mm i.d. x 6 mm o.d. and 4 mm i.d. x 6 mm o.d., respectively. The microtrap was packed with 60 mesh adsorbents. The adsorbent was held in place with small plugs of silanized glass wool. The microtrap has a resistance of about

0.1 Ω/cm. For a 0.53 mm id microtrap, about 30 mg adsorbent was packed. The microtrap was heated by passing current through the wall of the tube. The thin walled, small diameter tube has 1 gram of thermal mass and can be heated and cooled very rapidly. Before use, the microtraps were conditioned under zero grade nitrogen (6 ml/min) at 250 °C for 8 hr.

A Variac (STACO, PA) was used as the power supply, and two 5 Ω parallel power resistors (Dale RH-50, Israel) were placed in series with the microtrap to control the current through it. A microprocessor controlled electronic switch (built in-house) was used to control the heating time and injection interval. The duration of each pulse was approximately 1.2 second for 0.53 mm i.d. microtrap, and was longer for a larger size microtrap. The voltage of power supply was set at 30 volt.

3.2.2 Measurement of Breakthrough Volume

The apparatus used for the determination of breakthrough volumes is shown in Figure 13 and 14. A homemade VOC standard gas in air was connected to a three-way valve. One way went to microtrap and another to an empty stainless steel tube in which a flow rate controller was installed. A power supply and computer switch system were set up for heating microtrap [30]. The GC systems were HP 5890 II (Hewlett Packard, PA) and Varian 3400 with FID.

In the frontal analysis experiment (direct measurement, Figure 13), the standard gas passed through the connection tubing, directly into the FID detector, Then the three-way valve was switched so that the gas standard was routed through the microtrap. The sample eluting from the microtrap was monitored by the FID. The direct breakthrough time (t_b) was determined by measuring the time passing between the disappearance of the FID signal due to the adsorption of the organics in the trap and the inflexion point of the curve when the t_b was attained (Figure 7).

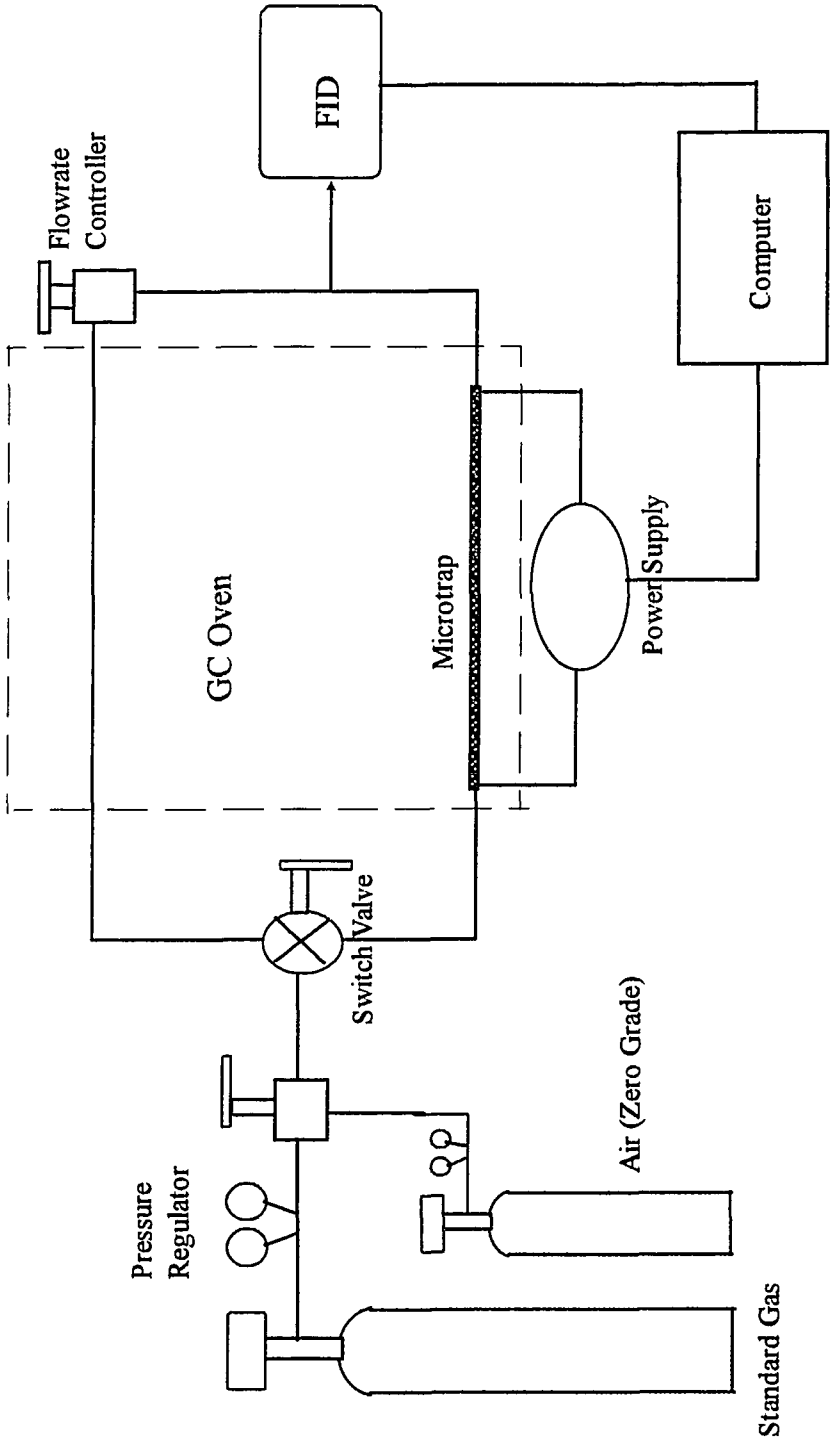


Figure 13 Schematic view of the apparatus for frontal analysis for the determination of breakthrough volume

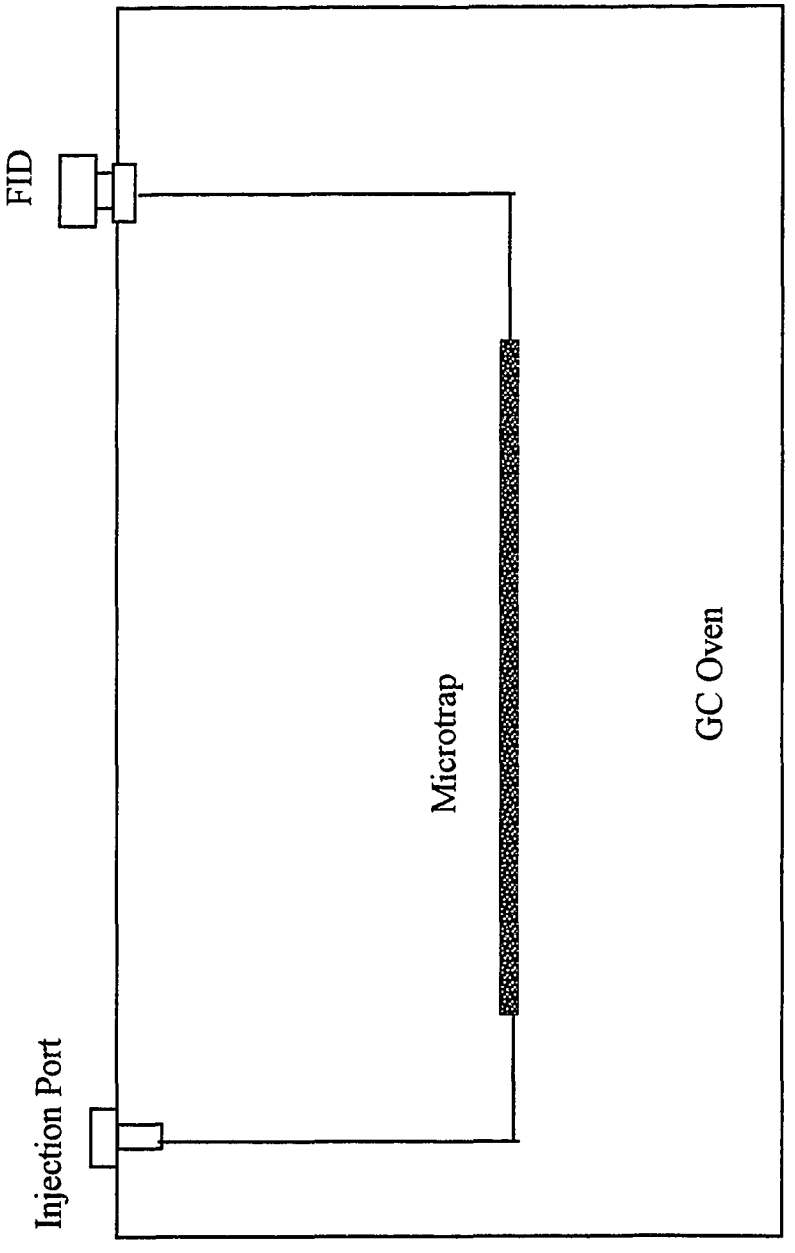


Figure 14 GC injection method for determination of breakthrough volume.

In the pulse interval method, the standard gas continuously flowed through the microtrap and for each interval a heating pulse is applied to the microtrap to release the analyte to FID detector. The peak areas were recorded at each interval pulse and a plot of peak area against pulse interval time was made. The time at the inflexion of the curve was the breakthrough time.

In GC injection method (indirect method, Figure 14), a 1 μl of sample headspace was injected into the microtrap. The effluent at the end of microtrap was monitored by FID.

The breakthrough volume (V_b) can be calculated as follows [72]:

$$V_b = \text{milliliters of gas needed to cause adsorbate to migrate} = (F_c)(j)\,(t_b - t_o) \quad (3.1)$$

where

$$j = \frac{3}{2}\left[\frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1}\right]$$

$$F_c = (F_0)\left[\frac{T_c}{T_0}\right]\left[1 - \frac{P_w}{P_0}\right]$$

t_b = breakthrough time (min)

t_0 = retention time for dead volume (min)

P_i = inlet pressure of the microtrap (psi)

P_0 = outlet pressure (ambient pressure) (psi)

F_0 = flow rate measured in the outlet by a bubble meter (ml/min)

T_c = oven temperature (K)

T_0 = ambient temperature (K)

P_w = vapor pressure of water (psi)

3.2.3 Measurement of Theoretical Plate Number

A microtrap was installed in GC oven between the injection port and FID detector of GC. 1 μl of head space of pure organics liquid was injected into a split injector

(1:20) and the effluent of the microtrap was monitored. The theoretical plate number (N) can be calculated by [59]:

$$N = 5.54(\frac{t_R}{W_{1/2}})^2 \quad (3.2)$$

where t_R is retention time; $W_{1/2}$ is the peak width at half height.

An averaged theoretical plate number at three different temperatures was used in this study.

3.3 Results and Discussion

Since the microtrap is designed as an on-line preconcentrator and injection device for continuous analysis, three things influence the performance of the microtrap: trapping efficiency, thermal desorption efficiency and desorption speed. In ideal conditions, the trapping and desorption efficiency is 100% and the desorption speed is fast enough (less than 1 second) to provide sharp chromatographic injections and keep high separation efficiency of the column. The microtrap has similar adsorption and desorption mechanism as a sorbent trap. But the microtrap has a specific operation mode and different functions from a conventional sorbent trap.

3.3.1 Trapping Theory of On-line Microtrap

A typical configuration of microtrap was on-line microtrap system in which the microtrap was placed at the front of the analytical column [30]. In this system, the sample stream continuously flowed through the microtrap and at predetermined intervals, a heating pulse was applied to desorb the trapped VOCs into the GC column. The trapping efficiency (T) can be defined as the ratio of trapped samples to total sample passing through it. Assuming that the capacity factor of the analytes is close to zero when a pulse heating is given to the microtrap, the trapping efficiency (T) can be calculated as follows [30, 60]:

$$T = \frac{\text{the trapped amount of sample}}{\text{the total amount of sample passing through}} \cdot 100$$
$$= \frac{F \cdot t_{eff} \cdot C'_{sample}}{F \cdot t_i \cdot C'_{sample}} \cdot 100 \qquad (3.3)$$
$$= \frac{t_{eff}}{t_i} \cdot 100$$

where t_{eff} is the effective time for the microtrap to trap the analytes quantitatively; t_i is the interval time between two injections and equals the sampling time at which the sample passes through the trap, F is the volumetric flow rate of the sample through the trap; C'_{sample} is the concentration of sample. The maximum t_{eff} is

$$t_{eff} = t_b - t_h \qquad (3.4)$$

where t_b is the breakthrough time. t_h is the time at which the microtrap is hot so that the capacity factor is close to zero and sample migrates at the speed of mobile phase. In ideal case, t_h can be the minimum time required for analytes to migrate out of the trap. Thus

$$t_h = L/\mu \qquad (3.5)$$

where L is the length of microtrap (cm) and μ is the linear velocity (cm/sec.), which is defined as the volumetric flowrate divided by the cross area of microtrap interception. In this case, when a typical microtrap is used and the flow rate of carrier gas is 4 ml/min, the t_h is less than 1 second.

When the pulse interval $t_i < t_b$, $t_{eff} = t_i - t_h$.

$$T\,(\%) = (1 - \frac{t_h}{t_i}) \cdot 100 \qquad (3.6)$$

Since $t_i >> t_h$ in most of applications, T is close to 100%. The trapping efficiency is not related to the capacity factor. Figure 15 presents a chromatogram of microtrap when the t_i is less than t_b. The chromatogram appears the same as an ordinary one and no "negative" peak occurred because there is no breakthrough during this time [30].

When the pulse interval $t_i = t_b$, $t_{eff} = t_b - t_h$

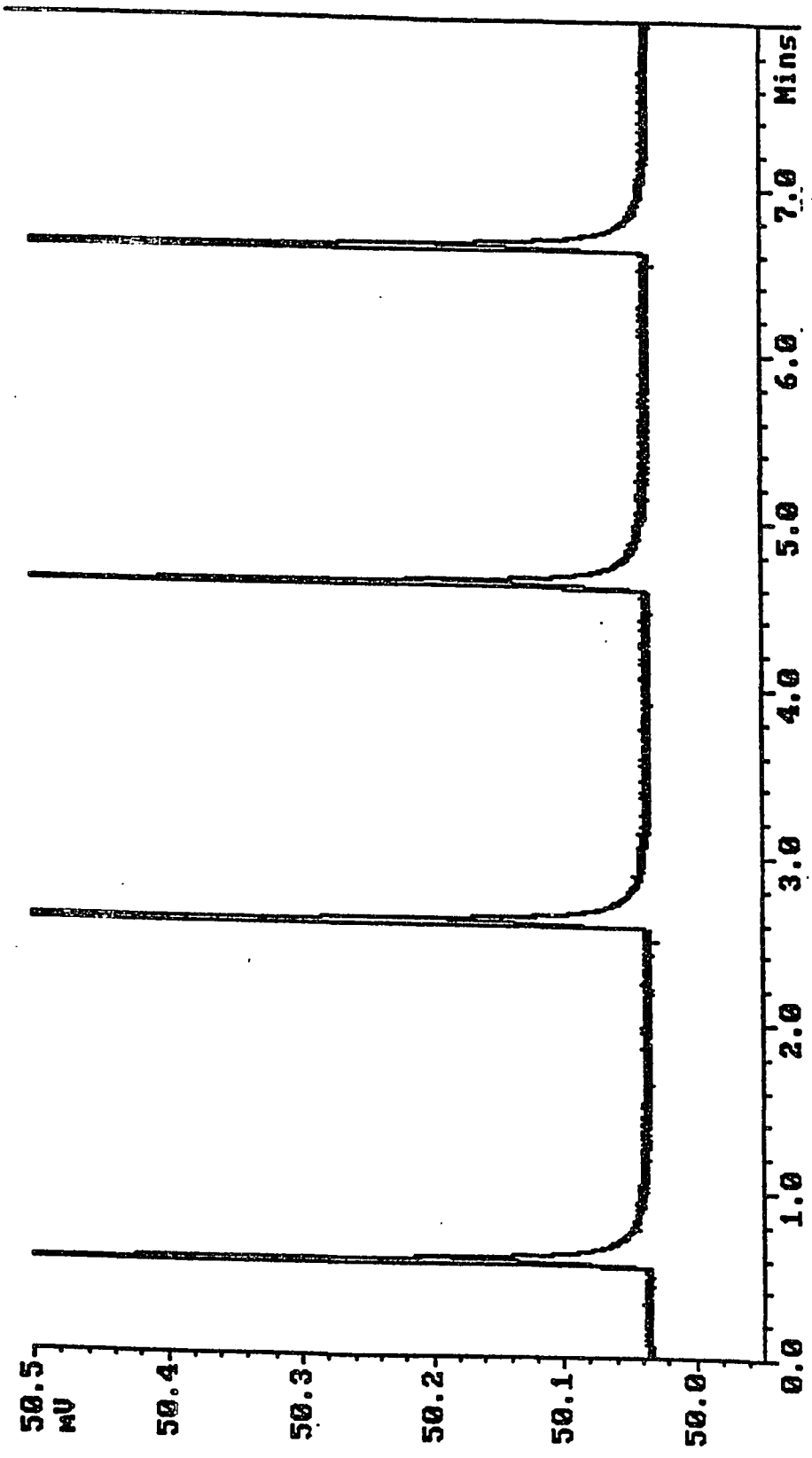


Figure 15 A typical chromatogram of on-line microtrap at $t_i < t_b$. A 6 inch long 0.53 mm i.d. microtrap packed with Carbotrap C was used. A standard gas containing 1 ppm of toluene was used and the pulse interval was 2 minutes.

$$T\ (\%) = (1 - \frac{t_h}{t_b}) \cdot 100 \tag{3.7}$$

If a GC injection method is used to measure the breakthrough volume, the migration of analytes in the microtrap can be described by column mechanism. When the breakthrough time (t_b) is close to the retention time (t_R), The time (t_b) at which a sample migrates through a microtrap is given by [30]:

$$t_b = (k + 1)L/\mu \tag{3.8}$$

By substituting Equation (3.5) and (3.8) into Equation (3.7):

$$T\ (\%) = k/(1+k) \tag{3.9}$$

Figure 16 presents the effect of capacity factor on trapping efficiency. When $t_i = t_b$, the trapping efficiency increases with the increasing capacity factor. But when the capacity factor is up to 30, this effect is not significant and the trapping efficiency is close to 100%.

When $t_i > t_b$, $t_{eff} = t_b - t_{hot}$. The trapping efficiency can be written:

$$T(\%) = \frac{t_b - t_{hot}}{t_i} \cdot 100 \tag{3.10}$$

By substituting Equation (3.5) and (3.8) into Equation (3.10):

$$T(\%) = \frac{Lk}{ut_i} 100 \tag{3.11}$$

In this case, the trapping efficiency is inversely proportional to the interval time between pulses and is proportional to the capacity factor. Moreover, a "negative" peak appears in the chromatogram (Figure 17). This is because some analytes break through the OLMT when $t_i > t_b$. Since the sample stream was a part of the carrier gas in OLMT system, untrapped analytes directly flowed through FID and contributed to the increase of the detector baseline.

3.3.2 Determination of Breakthrough Volume

Previous work [60] showed that linear calibration curves can be obtained in both of the interval test regions. However, some specific applications require total

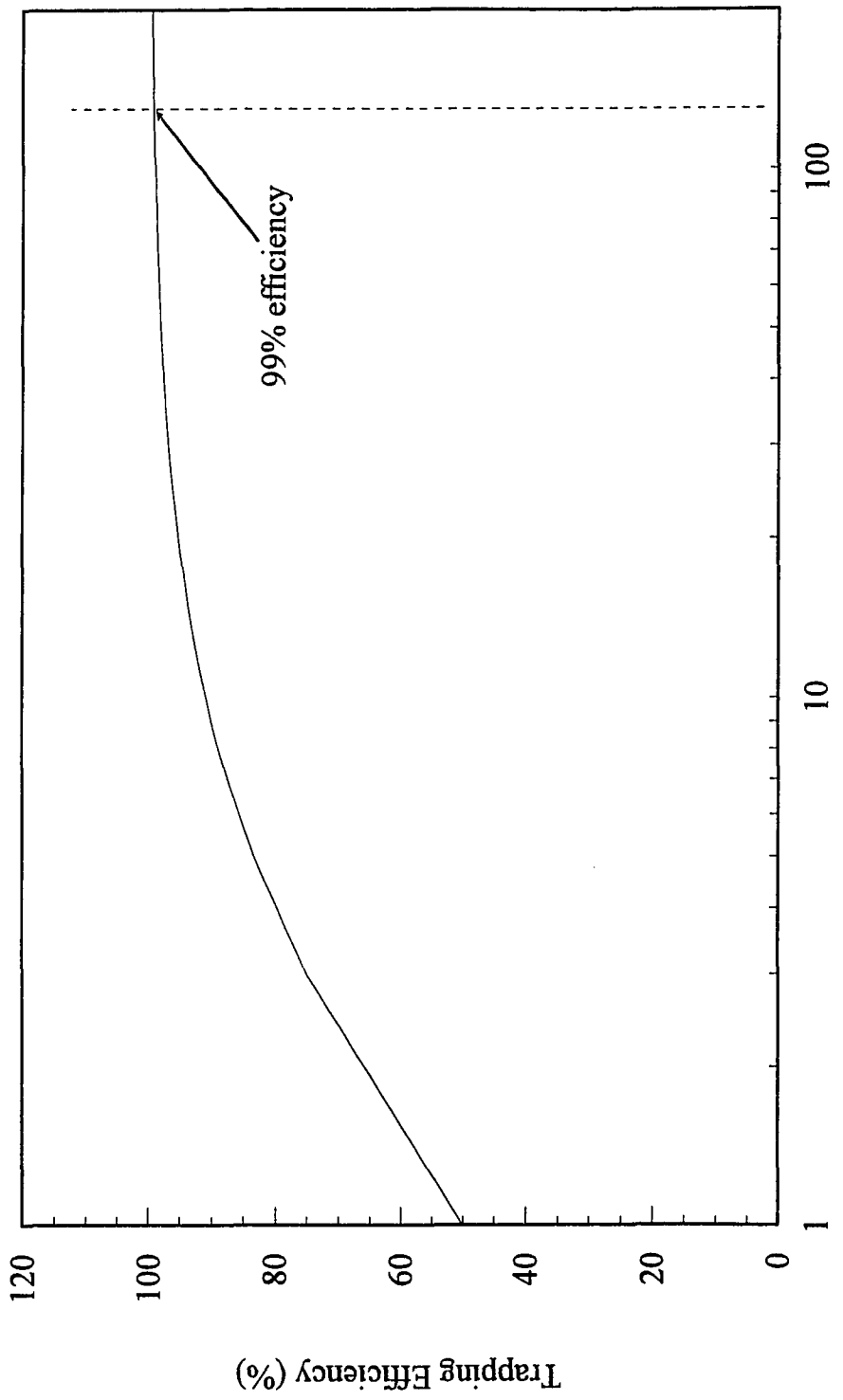
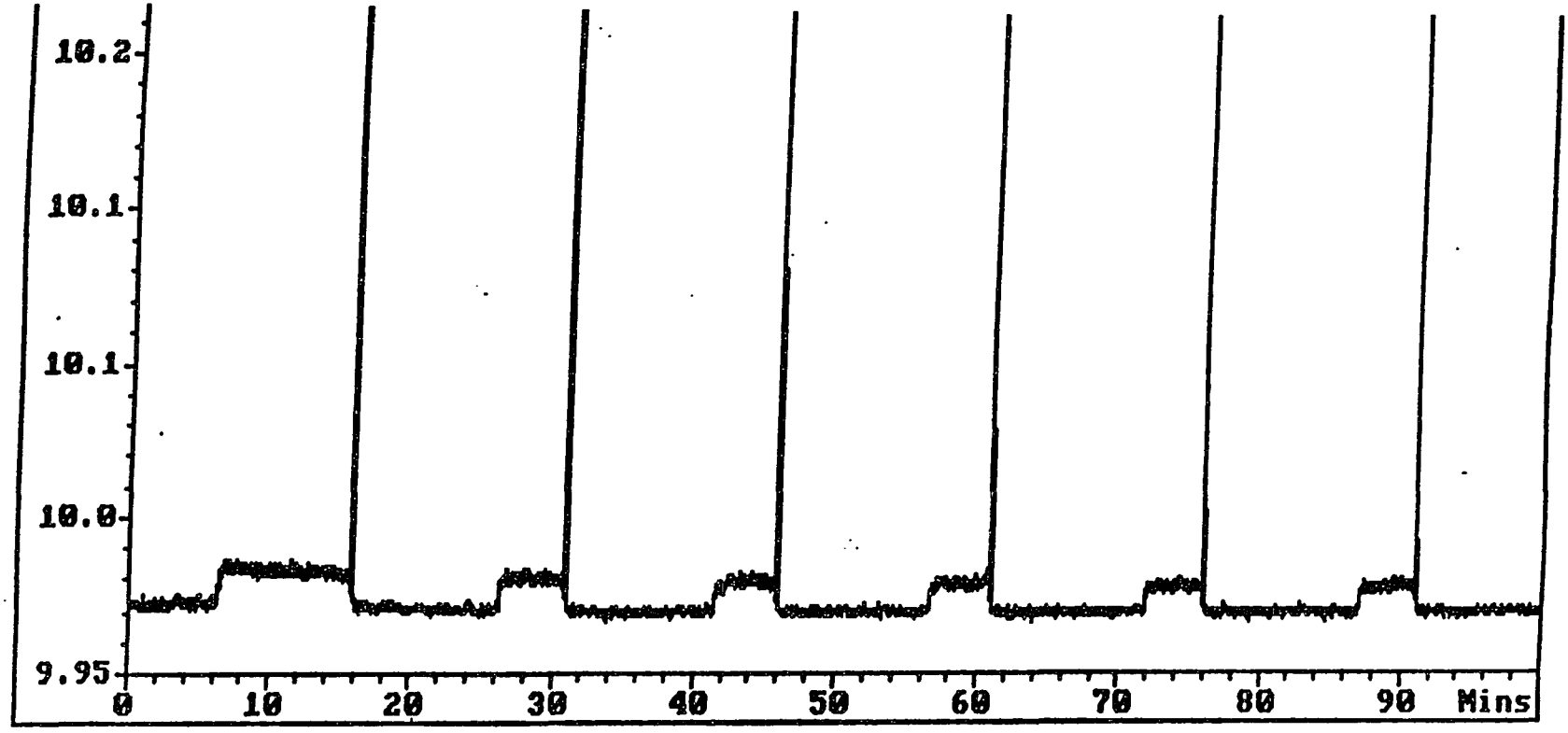


Figure 16 Effect of capacity factor on trapping efficiency when $t_i = t_b$



Time (min)

Figure 17 A typical chromatogram of continuous monitoring using on-line microtrap system at $t_i > t_b$. A 6 inch long 0.53 mm i.d. microtrap packed with Carbotrap C was used. A standard gas containing 1 ppm of toluene was used and the pulse interval was 15 minutes.

trapping efficiency to achieve the required analytical accuracy. Thus the pulse interval has to be less than breakthrough time. So, the investigation of breakthrough characteristics of microtrap is crucial for microtrap applications.

Frontal analysis is a classic method for the measurement of breakthrough volume/time. However the microtrap has small diameter and has relative high pressure drop. Figure 18a shows a typical chromatogram of frontal analysis in the microtrap system. It is seen that the chromatogram is unstable when three way valve switches to the microtrap. This may be caused by disturbing the system since it takes almost one minute for flow rate to reach an equilibrium. This may be caused by the analyte diffusion from tubing to the detector. The pulsed frontal experiment was also used to measure the breakthrough time. Since no gas stream direction was switched/changed, the flow rate was not disturbed and remained constant. The chromatogram of pulsed frontal experiment is presented in Figure 18b. We tested several compounds at different flow rates. These two methods gave same results. Table 3 lists the breakthrough volume for some VOCs using these two methods. The heating period of microtrap has no significant effect on results since the heating\cooling cycle only takes a few seconds.

Table 3. Breakthrough Volume of Some VOCs [1]

Compounds	V_b (ml) by Frontal Analysis	V_b (ml) by Pulse Frontal Analysis
Toluene[2]	90	88
Trichloroethylene[3]	38	37
Hexane[4]	53	52

Note: [1] A 6 inch long, 0.53 mm i.d. microtrap packed with 30 mg Carbotrap C was used.

[2] The concentration of toluene was 0.2 ppm_v and the temperature of microtrap was 60 °C.

[3] The concentration of trichloroethylene was 1.5 ppm_v and the temperature of microtrap was 30 °C.

[4] The concentration of hexane was 2.2 ppm_v and the temperature of microtrap was 30 °C.

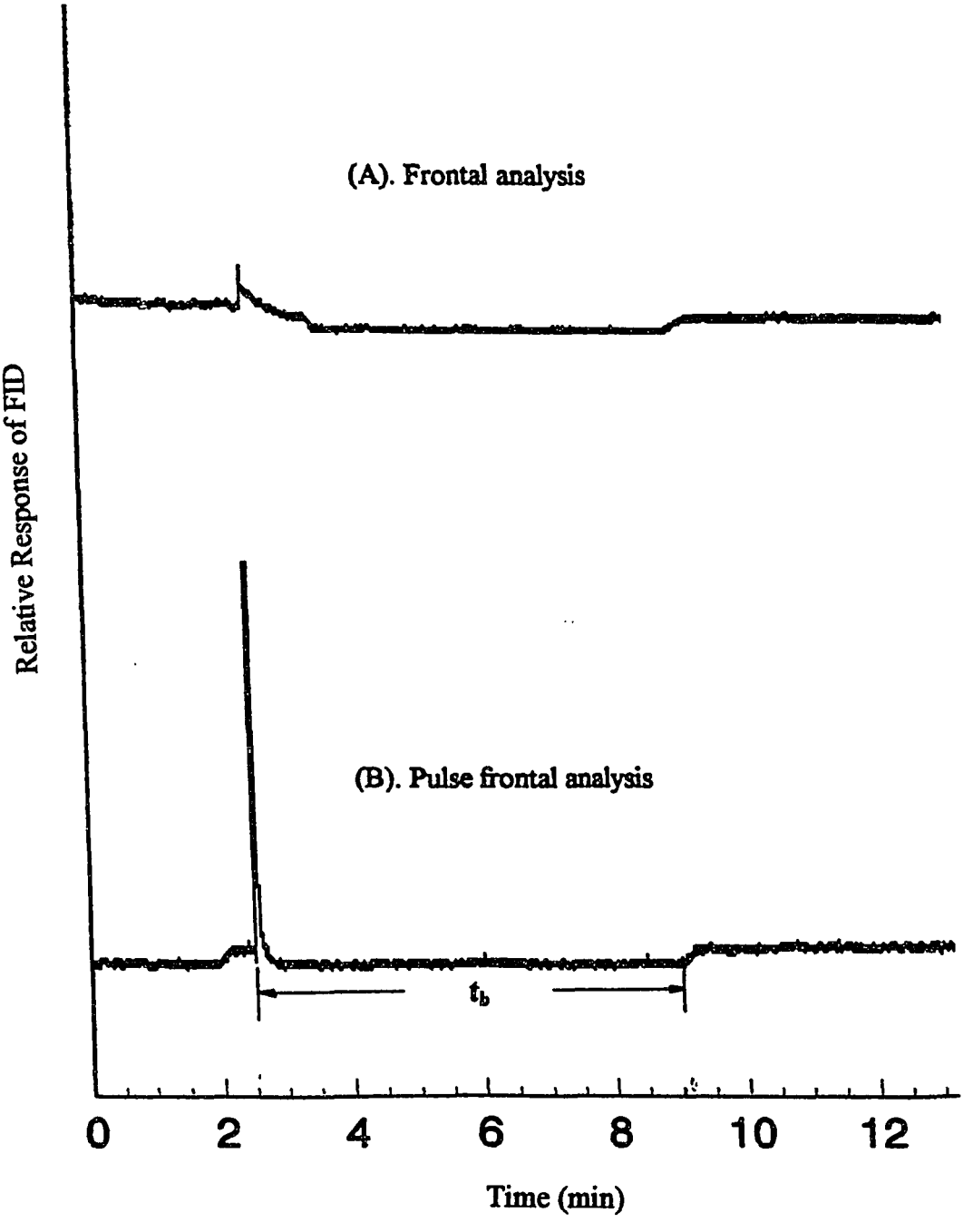


Figure 18 Chromatograms for the determination of breakthrough volume using frontal analysis and pulse frontal analysis. A 6 inch long 0.53 mm i.d. microtrap packed with Carbotrap C was used. A standard gas containing 1 ppm of hexane was used.

When the concentration of analyte in gas stream is lower than 20 ppb, it is very difficult to determine the breakthrough time using the negative peak in the frontal or pulsed frontal experiment, because the FID signal is too small and the changes can not be seen clearly. But the microtrap is designed for trace analysis and the characteristics of breakthrough at low ppb range are of most concern. Here, a pulsed interval experiment was used to measure the breakthrough time at low concentration. In the interval experiment, the analyte gas stream continuously passed through microtrap. After interval, a heating pulse is applied to release the trapped analyte into detector. Different responses can be obtained with the change of pulse interval time [60]. Figure 19 has shown the plot of peak area against pulse interval. The inflexion point of this curve is the breakthrough point. The experiment results showed the breakthrough volume determined by the interval experiments was a perfect match to that obtained by the frontal experiment in the range of 200 ppb to high ppm. Furthermore, the interval test is an alternative method for frontal experiment and has advantages over conventional frontal experiment in very low concentration ranges (low ppb).

3.3.3 Parameters Effecting the Breakthrough Volume

1. Effect of The Microtrap Size

The dimensions of a typical microtrap are 0.029" o.d. and 0.021" i.d., while the common sorbent trap is 1/4-in o.d. and 0.17-in i.d.. Figure 20 presents the Van Deemter plots for different trap sizes. The number of theoretical plates of the traps did vary significantly with flow rate and increased with decrease of inner diameter of trap, as expected from the Van Deemter equation [61].

Under fixed conditions, the retention volume is constant and would not be affected by the plate number. However, the breakthrough volume (as we have defined it) will be less than the retention time, because the column efficiency of the microtrap must be taken into account. According to integrals method outlined

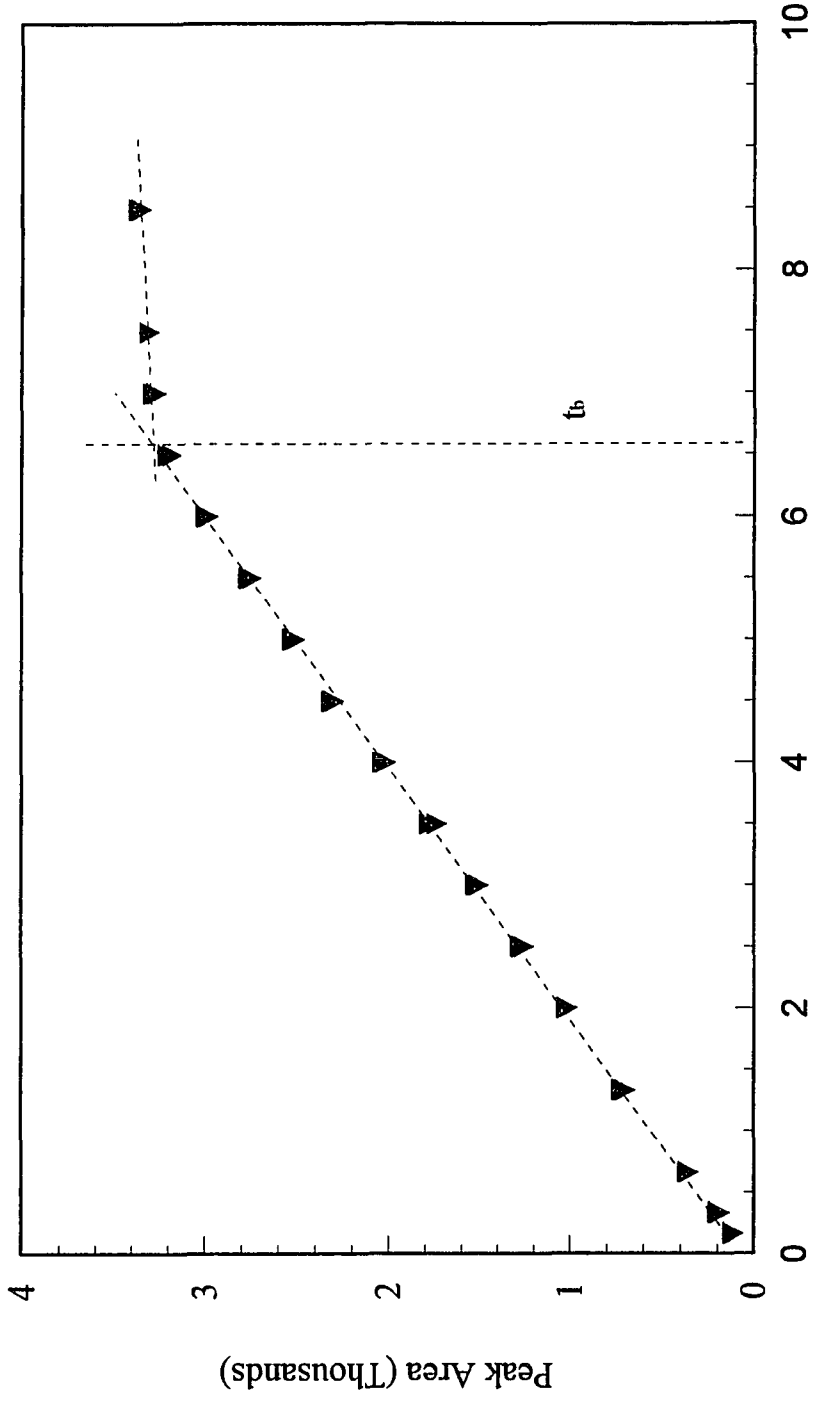


Figure 19 Plot of peak area against pulse intervals. A 6 inch long, 0.53 mm id microtrap packed with Carbotrap C was used. A standard gas containing 1 ppm of hexane was used and the flow rate was 5 ml/min. The microtrap temperature was 35°C.

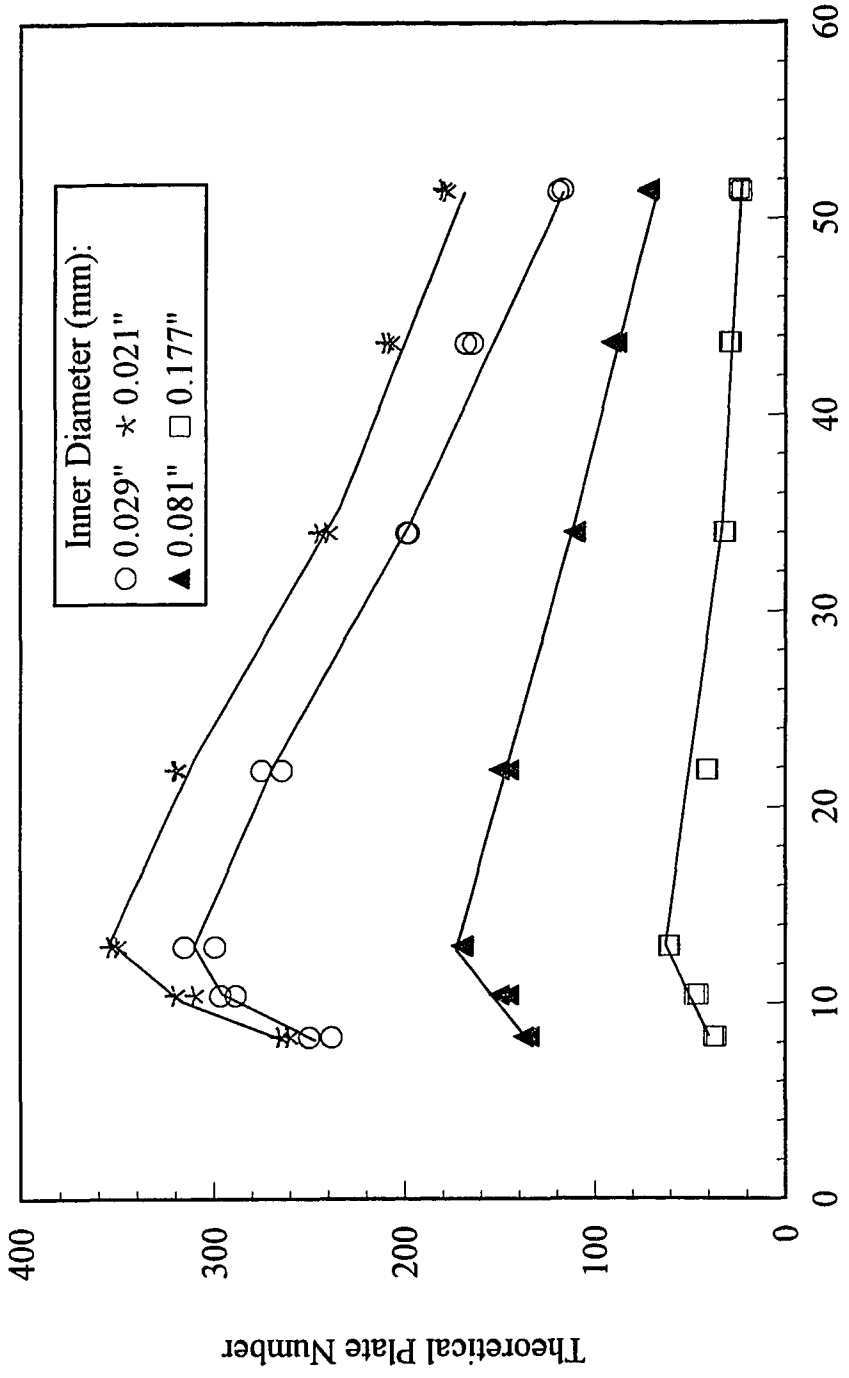


Figure 20 Van Deemter plot for different size microtraps. 6 inch long microtraps were packed with 60 mesh Carbotrap C and nitrogen was used as carrier gas. The theoretical plate number at each flowrate was obtained by averaging number at three different temperature.

by Cropper and Kaminsky [34], assume the sampling volume (V_s) = the retention volume (V_R). the number of units of a component which are not trapped is expressed as:

$$i_{lost} = \sum_{i=0}^{100}\left[0.5 - \frac{1}{\sqrt{2\pi}}\int_0^t \exp(-\frac{t^2}{2})dt\right] \tag{3.12}$$

where $t = i/\sigma$,The standard deviation, σ, is

$$\sigma = V_R/\sqrt{N} \tag{3.13}$$

where V_R is the retention volume (equal to 100 units) and N is the theoretical plates number of the microtrap. In this case, the trapping efficiency (the sampling efficiency) = (100 - i_{lost}).

When the sampling volume V_s =(1- j/100)/ V_R , equation 3.12 becomes:

$$i_{lost} = \sum_{j}^{100}\left[0.5 - \frac{1}{\sqrt{2\pi}}\int_0^t \exp(-\frac{t^2}{2})dt\right] \tag{3.14}$$

where, j = the percentage of unsampled retention volume. The trapping efficiency can be calculated as follows:

$$\text{Trapping Efficiency} = \frac{(i_{sampled} - i_{lost})}{i_{sampled}} x\ 100\% \tag{3.15}$$

where $i_{sampled}$ = 100 - j.

Figure 21 gives the plot of breakthrough volume as a fraction of the retention volume as a function of microtrap theoretical plate number (calculated using MatLab program. See Appendix A). When the plate number increases the breakthrough volume increases significantly. When the plate number is 150 or larger, the breakthrough volume is close to the retention time. If we define the breakthrough volume as the sampling volume at 95% efficiency, the breakthrough volume is almost the same as the retention volume when the plate number is 100 or larger. For the typical microtrap (0.021" i.d.), the number of theoretical plates is larger than 150 in the flow rate range of 0.8 ~ 20 ml/min. Thus, the breakthrough volume is close to the retention time in the microtrap. For a common sorbent trap

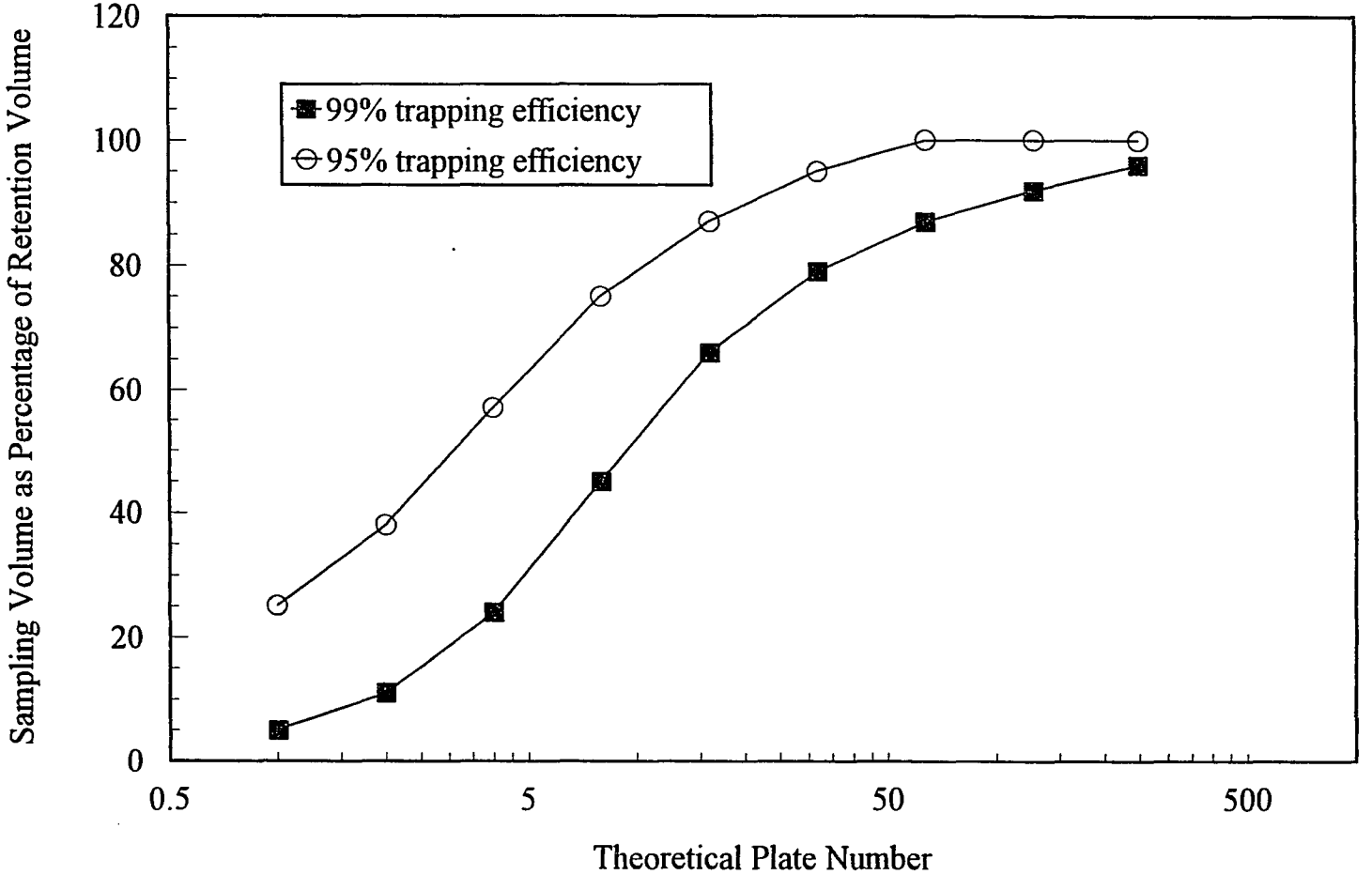


Figure 21 Plot of sampling volume as percentage of retention volume as a function of theoretical plate number.

(1.77 inch i.d.), the maximum number of plates is only 60 at optimal sampling flow rate. The breakthrough volume is only 85% of retention volume. Thus for the microtrap, we can use the retention volume as breakthrough volume when the breakthrough time and the pulse interval are considered.

Therefore the microtrap should have a small diameters and be about 6 inches long to provide enough plates. In addition, a thin tube has small thermal mass so that it is heated or cooled very rapidly. However, a very thin microtrap is difficult to pack. Considering the plate number and packing problem, an inner diameter of about 0.75 mm is suitable.

2. Effect of Analyte Concentration

The microtrap is designed for trace organic analysis. So, in this study the concentration of analyte was limited to the range of 10 ppb to 4 ppm. In a direct injection GC method, the concentration effect on breakthrough volume is ignored. However, the concentration of analyte does affect the breakthrough volume. In this experiment, the breakthrough volumes were determined by pulse frontal analysis and the interval test. Figure 22 presents the relationship between breakthrough volume and analyte concentration. The breakthrough volume decreases significantly with the increase of the analyte concentration. This relationship in the test concentration range can be described by the following the equation:

$$V_b = - K\log C + B \qquad (3.14)$$

Thus, when the breakthrough volume of analyte at low concentration is sought, frontal analysis or interval test should be used to determine it. A single pulse injection method sometimes gives false results since it ignores the concentration effect [62].

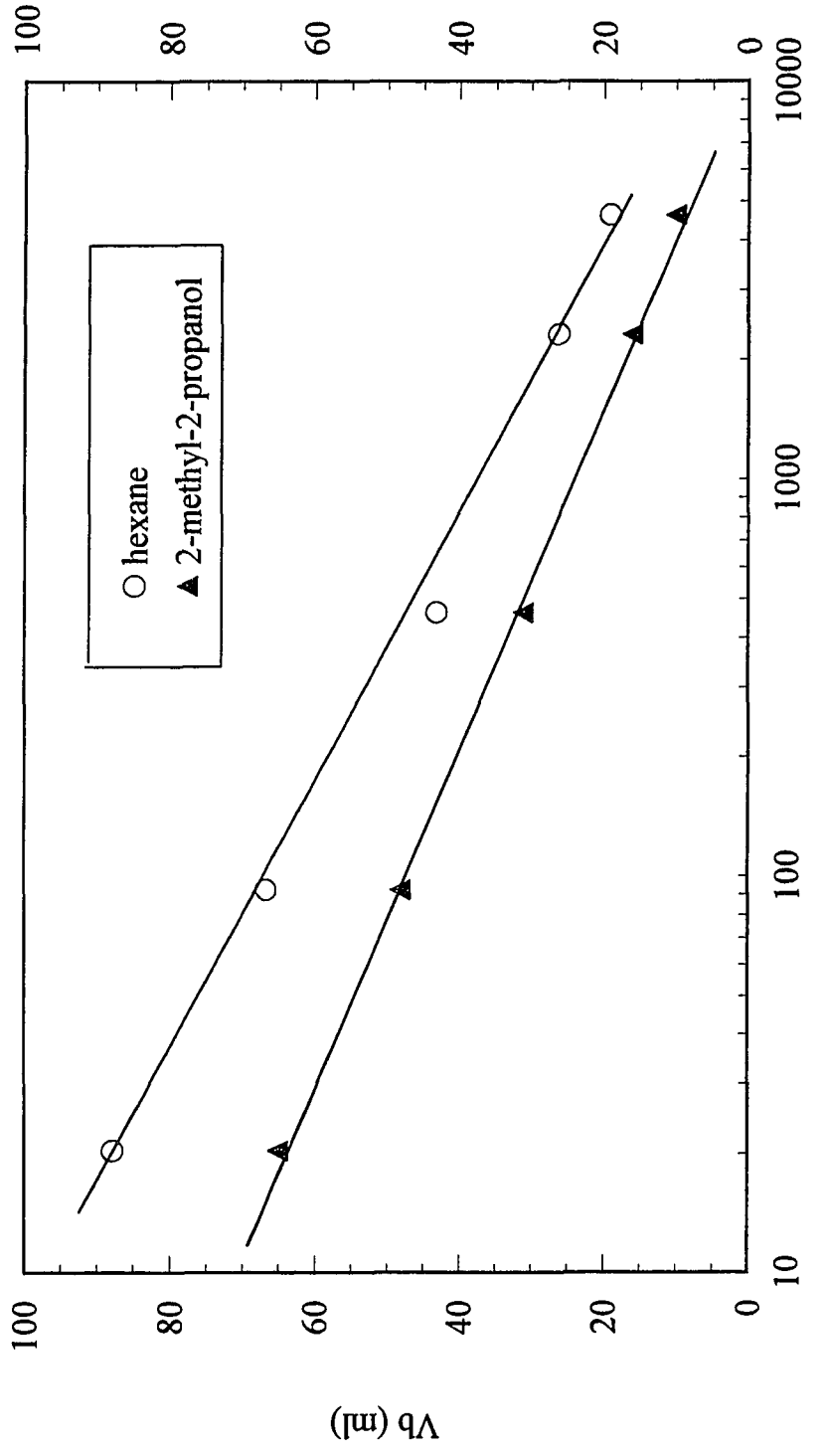


Figure 22 Plot of breakthrough volume against the concentration. A 6 inch long 0.53 mm id microtrap packed with Carbotrap C was used and the microtrap temperature was 30°C.

3. Effect of Operating Temperature

Temperature is one of the crucial parameters which affects the breakthrough volume since capacity factors decrease with an increase in temperature. Figure 23 presents the results. In fact, the breakthrough volume at 20 °C in most literature was obtained by extrapolation of this straight line [62, 63].

In the analytical operation, the microtrap is held at ambient temperature. Thus, room temperature variation will cause changes in the breakthrough volume. However, this variation of breakthrough volume does not influence the response and trapping efficiency, if the breakthrough time still is larger than pulse interval, even if the operating temperature fluctuates. Figure 24 presents the effect of microtrap temperature on system response. For chlorobenzene, the response remains constant even though the microtrap temperature varied from 30 °C to 70 °C. For chloroform, the response decreased significantly with the increase in temperature. These results were expected because chlorobenzene has a larger breakthrough volume than chloroform. Even through the microtrap temperature varied from 30 °C to 70 °C, the breakthrough time of chlorobenzene is still larger than interval time. Thus no decreased response for chlorobenzene occurred in this temperature range. For chloroform, the breakthrough time is less than the interval time in this temperature range. When the microtrap temperature increased, the breakthrough time decreased. Thus according to equation (3.10), the trapping efficiency decreased and the response decreased consequently.

4. Effect of Flowrate

The number of theoretical plates of the microtrap did vary significantly with flow rate. But the number of theoretical plates of microtrap is still higher than that of sorbent trap in our experimental range of flow rate. No significant variation of breakthrough volume with change of flow-rate was observed. Figure 25 shows the experimental and theoretical data on breakthrough volume.

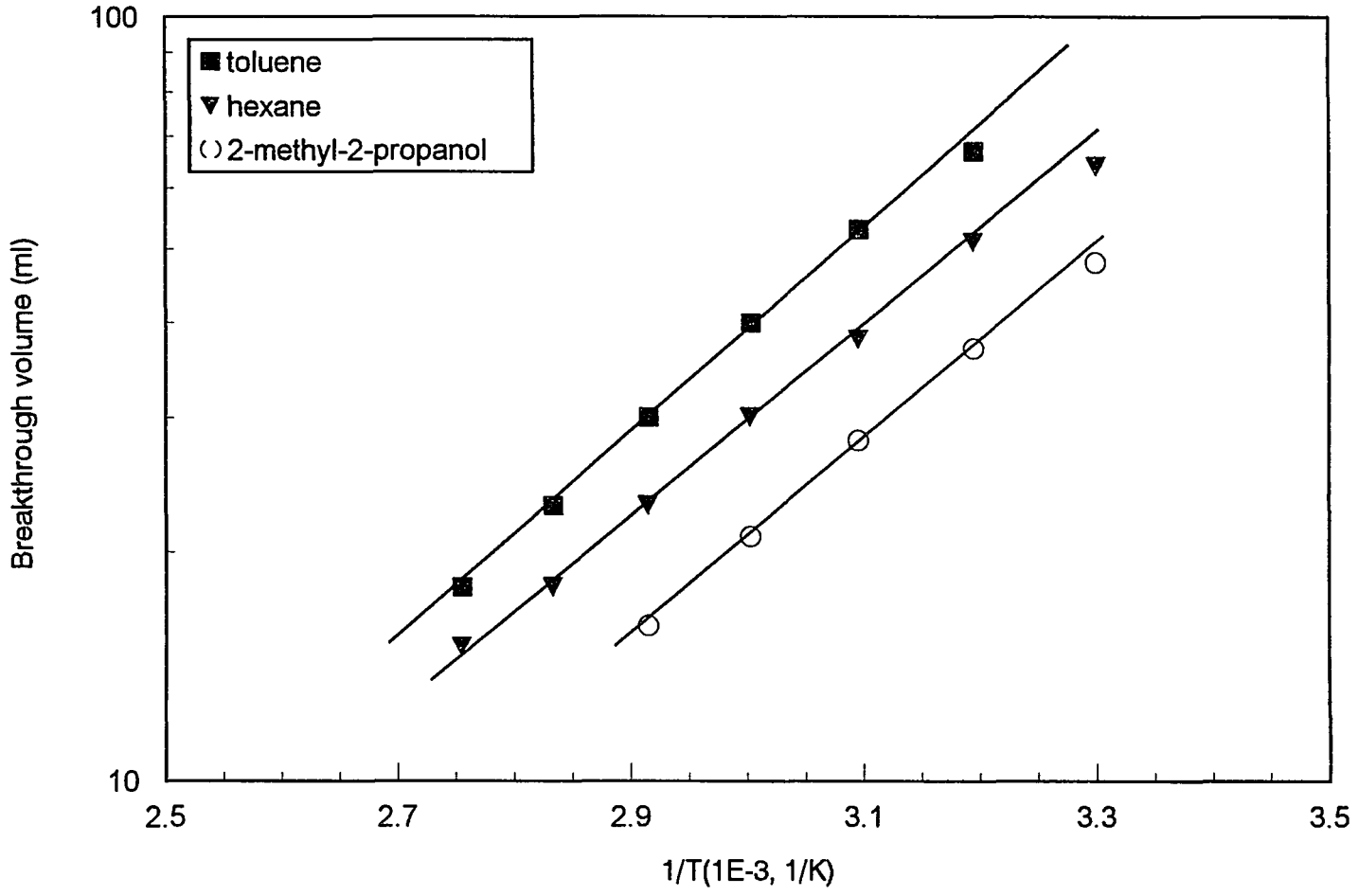


Figure 23 Effect of temperature on the breakthrough volume. A 6 inch long 0.53 mm id microtrap packed with Carbotrap was used. The injection method was used for the determination of breakthrough volume. The flow rate of carrier gas was 6 ml/min.

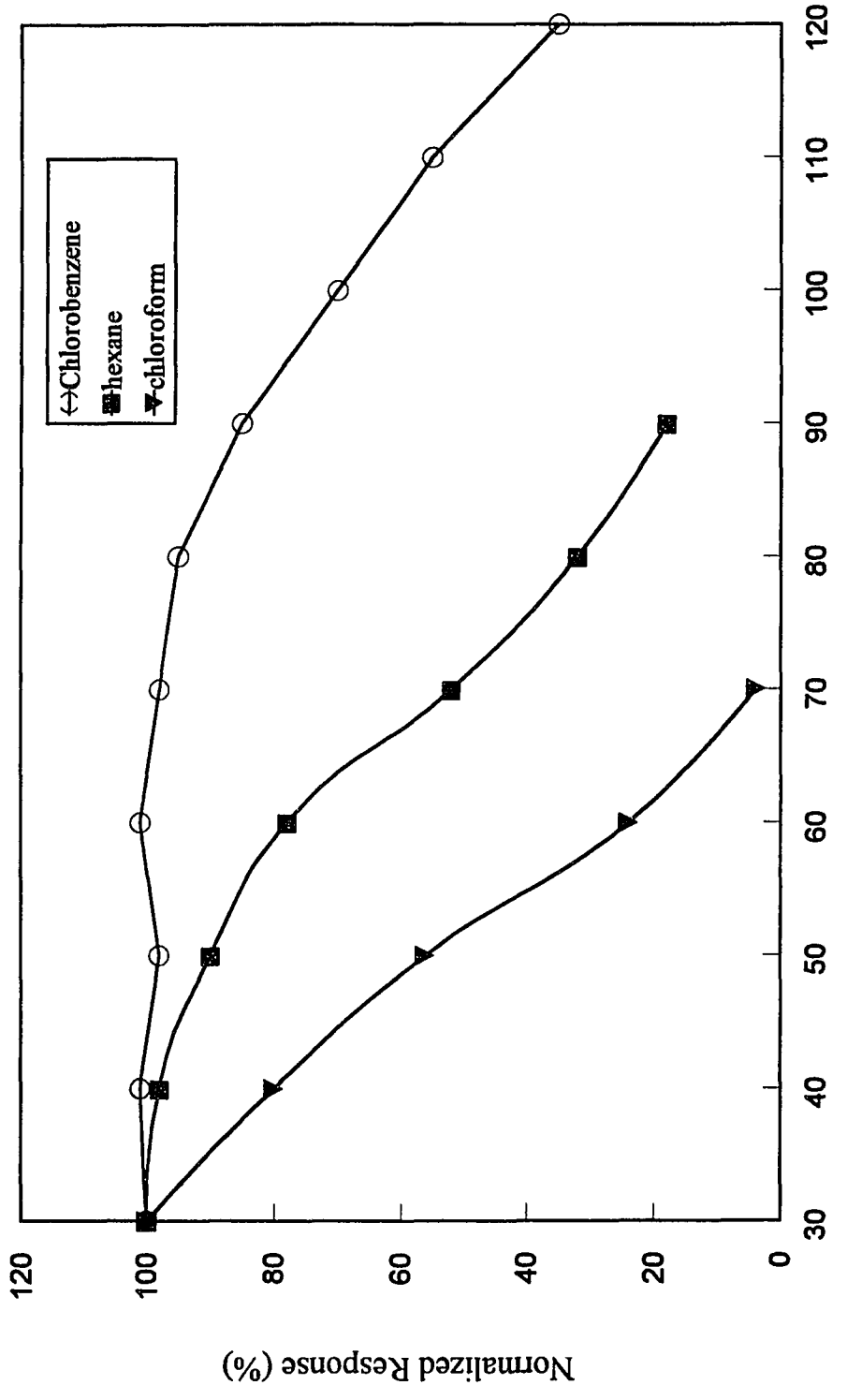


Figure 24 Effect of microtrap temperature on response. A 6 inch long 0.53 mm microtrap packed with Carbotrap C was used. The interval time was 2 minutes and the flow rate was 6 ml/min.

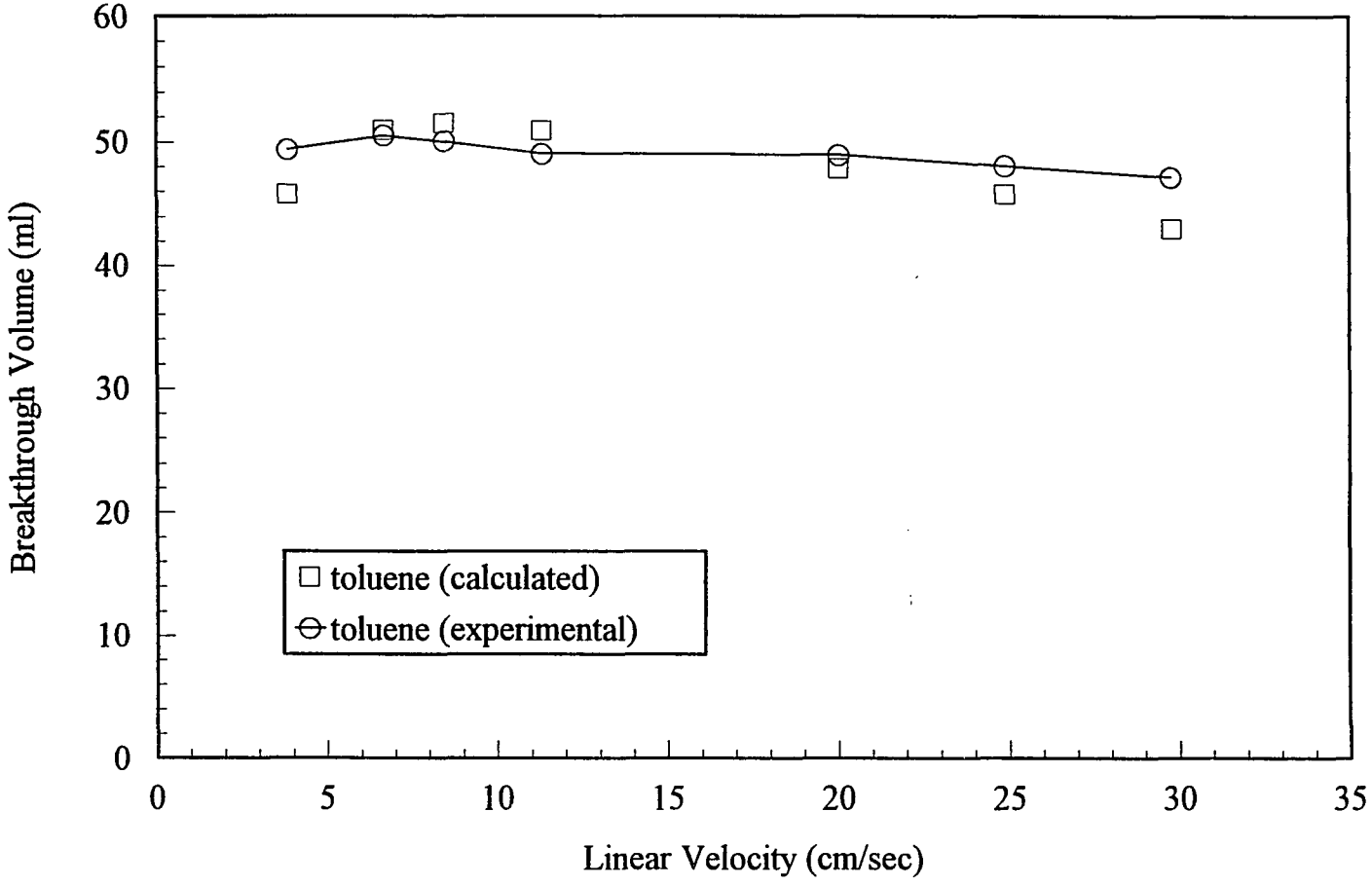


Figure 25 Effect of flow rate on the breakthrough volume. A 6 inch long 0.53 mm id microtrap was used and the amount of Carbotrap C in microtrap was 30 mg. The concentration of toluene (in nitrogen) was 1 ppm and the microtrap temperature was 70°C.

3.3.4 Design of A Multibed Microtrap

Environmental Protection Agency (EPA) VOCs list contains more than forty organics which range from vinyl chloride to xylene. A single bed microtrap cannot have high trapping efficiency and high desorption efficiency for all of the listed VOCs since a weak adsorbent has very small breakthrough volume for light VOCs and heavy VOCs may be difficult to desorb from a strong adsorbent.

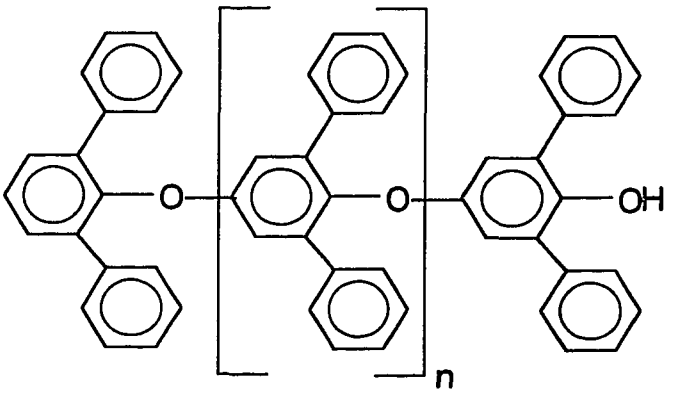
1. Adsorbents

The ideal sampling adsorbent will have a large capacity at ambient temperature for lightest target compounds and allow complete desorption of the heavy analytes by heating [64]. Sampling capacity is determined by the retention volume and efficiency of the trapping column for the least retained compound. The rate of the desorption and of sample injection depends mainly on the maximum temperature achievable and the heating rate. Accordingly, the thermal stability of the adsorbent must be considered. For that reason, we have not considered supports coated with high-boiling liquid phases which would bleed and could even react with some of the compounds studied [65].

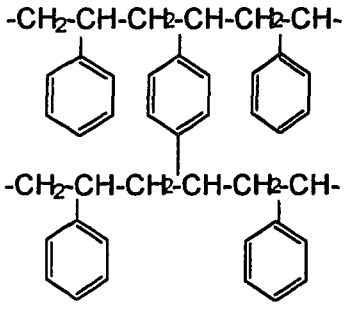
There are many commercially available adsorbents for air monitoring such as the porous polymer, Tenax™, Carbopack™ and Carbotrap™. It is convenient to classify adsorbents into basic types in accordance with the charge distribution at the surface [66]:

Type I, Nonspecific. The surface of this kind of adsorbent bears no functional groups or exchangeable ions. The typical examples are graphitized carbon black and saturated hydrocarbon polymer. These interact largely nonspecifically with all of samples.

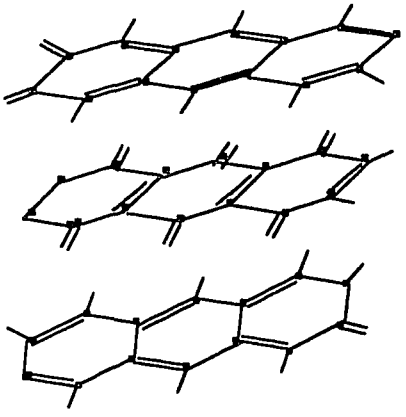
Type II, Specific, with localized positive charge. These adsorbents bear acidic OH groups, such as hydroxylated surfaces of acid oxides, in particular silica. Zeolite is another example of this kind of adsorbent. The positive charge is



(26a) Surface model for Tenax GC resin



(26b) Surface model for Amberlite XAD-2 resin



(26c) Surface model for Carbotrap adsorbent

Figure 26 The surface model of common adsorbents.

localized in exchangeable cations and the negative charge is distributed over the $(AlO_4)^-$ anions of the zeolite framework [67, 68].

Type III, Specific, with localized negative charge. This type of adsorbent is readily produced by deposition of compounds containing CN or oxygen bridge groups on a nonspecific adsorbent or by formation of functional groups by chemical modification [69].

Table 4. Physical Characteristics of Adsorbents

Adsorbent	Mesh Size	Surface Area (m^2/g)	Temperature limit (°C)	Density (g/ml)	Description
Activated charcoal	20/40	1070	400	0.44	Coconut based
Tenax™ GC	20/40	19	>300 *	0.61	Type III, polymer
Carbotrap™ C	20/40	12	>400	0.72	Type I, gcb
Carbotrap™ (B)	20/40	100	>400	0.38	Type I, gcb
Carbosieve™ S-III	60/80	820	>400	0.61	Approach Type I, cms

* up to 300 °C with oxygen free gas

Tenax™ GC and Amberlite™ XAD™-2 resins are widely used adsorbents for air monitoring. They have localized surface charges for specific adsorbent /adsorbate interaction. Their chemical structures [70] are presented in Figure 26a, 26b. Carbotrap™ is one of several high purity, graphitized carbon black adsorbents. It can adsorb, then release a wide range of airborne organic contaminants. As a Class I adsorbent, it has no surface ions or active (functional) groups. The entire surface is available for interactions that depend solely on dispersion (London) force [71]. Furthermore, Carbotrap™ adsorbent is more hydrophobic in nature than either of the resins. Thus, its performance is unaffected by humidity. Carbotrap™ adsorbent is free of contaminants and is not susceptible to solvent degradation. Carbosieve™ is carbon molecular sieve and can have

surface characteristics that approach Class I categorization [72]. Due to their large surface area, carbon molecular sieves retain organic volatiles so strongly that a very high temperature would be necessary to desorb them and such conditions would cause pyrolysis of most compounds. Actually, carbon molecular sieves are designed for very light volatile compounds such vinyl chloride, propane and polar light organics [74, 75].

Table 4 presents basic properties of adsorbents [75] and Table 5 lists some data on breakthrough volume of typical adsorbents [76, 77, 78]. The breakthrough volumes are based on 30 milligrams of sorbent, the amount of adsorbent packed in a typical microtrap. From the data in Table 5, it is obvious that Carbotrap™ C is only able to trap very heavy organics while it has a small surface area (~12 m^2/g). Actually it has been used for trapping nonvolatile organics such as PCBs in foods and environmental samples, biological fluids or tissue [79]. Carbotrap™ (B) is suitable for middle sized organic compounds and has a surface area of 98.3 m^2/g. For Carbosieve™ S-III, the breakthrough volume of propane is 134.7 ml at 20 °C. When the flow rate passing through a microtrap is 6 ml/min, the breakthrough time is more than 20 minutes. Twenty minutes is enough for most applications. Thus, Carbosieve™ S-III is good for very light organics.

2. Multibed Microtrap

Microtrap injection may not be made very frequently in practical application due to the time limitation of column separation. It is suitable to make an injection for every 5 to 20 minutes in most cases. Therefore, to keep high trapping efficiency for light compounds, the breakthrough time t_b has to be large enough so that it is larger than the interval time between injections. To increase the breakthrough time for light compounds, either sub-ambient operating temperature or a stronger

Table 5. Breakthrough Volume Data at 20 °C (ml/30 mg) [67. 72, 73]

Compounds	Carbosieve™ S-III (30 mg)	Carbotrap™ B (30 mg)	Carbotrap™ C* (30 mg)
methane	0.255	N/A	N/A
ethane	2.919	0.519	N/A
propane	134.7	1.647	N/A
n-butane	906	12.18	0.1143
n-pentane	N/A	176.7	0.2505
n-hexane	N/A	2397	9.66
n-octane	N/A	480000	41.1
n-decane	N/A	14370000	390
n-dodecane	N/A	N/A	99000
methanol	71	N/A	N/A
ethanol	90.3	3.93	0.366
butanol	N/A	39	16.2
2-methyl-2-propanol	N/A	195.6	N/A
hexanol	N/A	420	64.2
octanol	N/A	7560	115.5
phenol	N/A	18480	N/A
p-cresol	N/A	618000	N/A
Vinyl Chloride	522	N/A	N/A
dichloromethane	5190	N/A	N/A
carbon tetrachloride	N/A	28.2	0.2157
1,2-dichloroethane	N/A	58.2	N/A
1,1,2-trichloroethylene	N/A	381	N/A
1,1,2-trichloroethane	N/A	741	N/A
chlorobenzene	N/A	47400	16.17
1,4-dichlorobenzene	N/A	402000	N/A
actone	264.6	20.52	3.9
2-butanone	N/A	112.8	18.9
cyclohexanone	N/A	61200	N/A
4-heptanone	N/A	73200	N/A
acetophenone	N/A	1920000	N/A
benzene	N/A	352.2	5.97
toluene	N/A	19500	23.31
ethylbenzene	N/A	609000	49.2
p-xylene	N/A	1281000	N/A
n-butylbenzene	N/A	17490000	N/A
biphenyl	N/A	N/A	3390
isopropylbenzene	N/A	5100000	N/A
n-propylbenzene	N/A	5160000	N/A
propionic acid	N/A	49.8	N/A
n-pentanoic acid	N/A	12930	N/A
n-butylamine	N/A	62400	N/A
benzylamine	N/A	669000	N/A

adsorbent can be used in the microtrap. Sub-ambient temperature operation is expensive, especially in continuous monitoring, and is not considered here. An absorbent with high surface area can be used for light compounds. But heavy compounds are difficult to desorb from a single strong absorbent microtrap. Thus a multi-bed microtrap was developed which contained three adsorbents with different adsorption affinities for various VOCs.

In a multi-bed microtrap, several different types of absorbents were packed into the trap in order of increasing absorbent affinity. The breakthrough time t_b can be expressed:

$$t_b = \sum t_i = \frac{L_1}{\mu}(1+k_1)+\frac{L_2}{\mu}(1+k_2)+\cdots+\frac{L_n}{\mu}(1+k_n) \qquad (3.15)$$

where $k_1<k_2<k_3 \ldots k_n$; $\sum L_i = L$.

In our multibed microtrap, Carbotrap™ C and Carbotrap™ (B) and Carbosieve™ S-III were used (Figure 27). At sampling, the Carbotrap™ C end is the inlet. Thus, as a sample stream which contains a variety of organic compounds passes through a multi-bed microtrap, the heavy compounds will be trapped by Carbotrap™ C and light compounds would break through from Carbotrap™ C. But they will be retained by Carbotrap™ (B) and Carbosieve™ S-III which have larger surface area. So the breakthrough time of light compounds in multibed microtrap is much larger than that in single bed (Carbotrap™ C) microtrap.

Figure 28 presents the effect of delay time on trapping efficiency. In this experiment, 100 μl of 1 ppm of standard gas was injected into the microtrap. Then, after a delay time, a electric pulse was applied to the microtrap. Each peak area was recorded and the trapping efficiency was calculated as follows:

$$\text{Trapping efficiency (\%)} = \frac{\text{Peak area at delay time}}{\text{Peak area at 30 second delay time}} \times 100 \qquad (3.16)$$

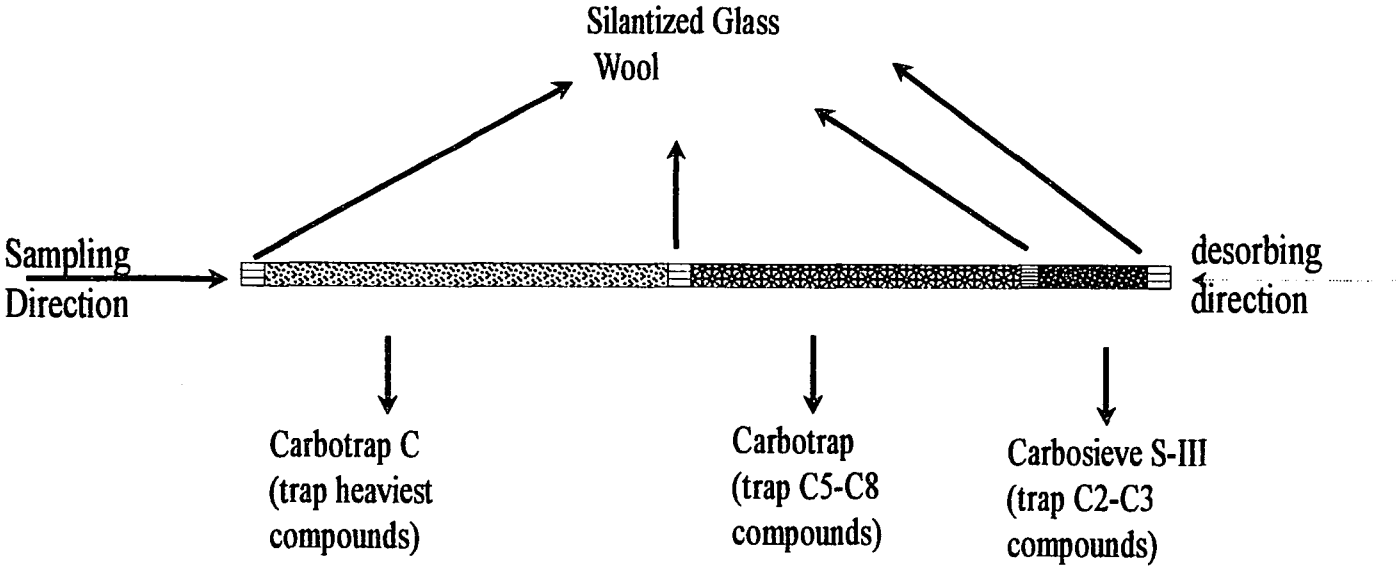


Figure 27 Diagram of a multibed microtrap

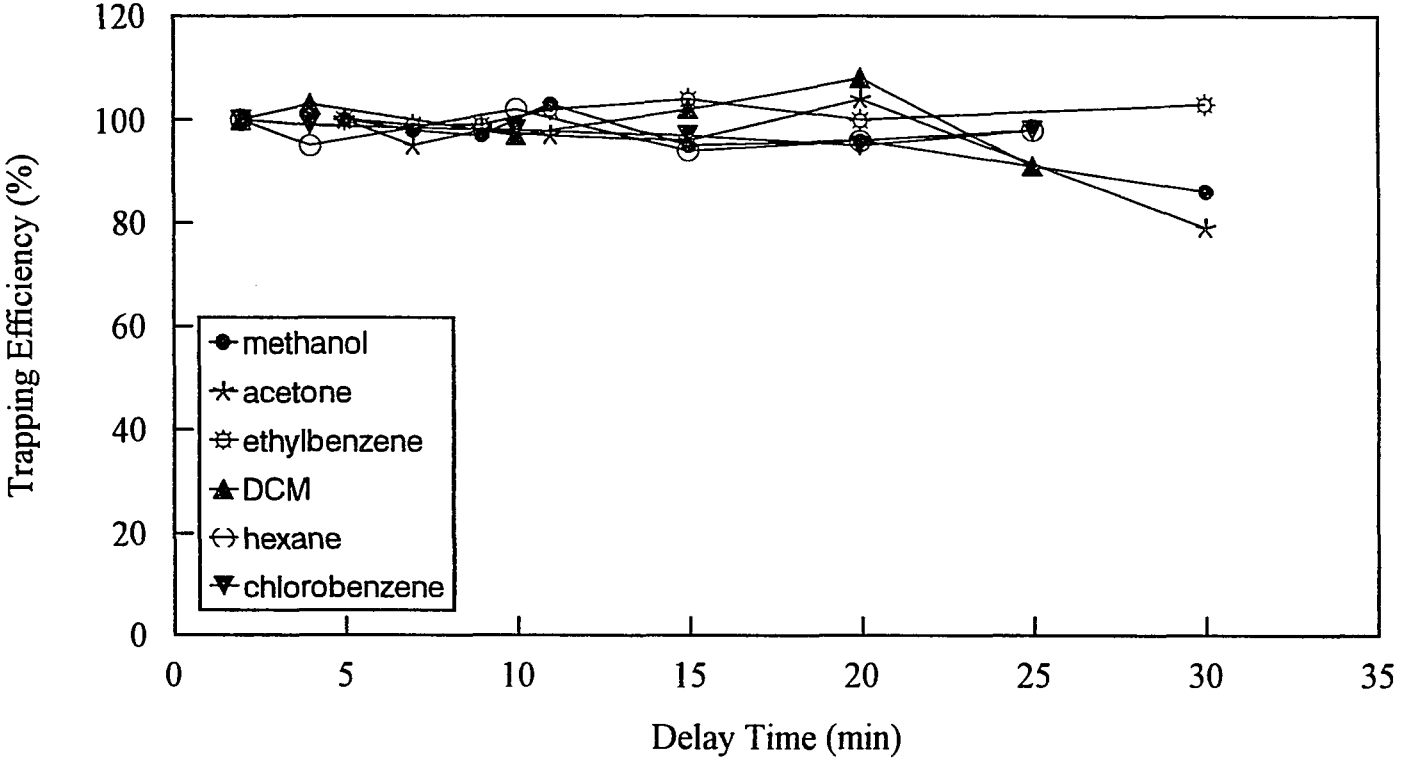


Figure 28 Effect of delay time on trapping efficiency. A 6 inch long 0.74 mm id microtrap packed with Carbotrap C, Carbotrap (B) and Carbosieve S-III in series was used. The flow rate was 10 ml/min.

In Figure 28 we observe, even for very light compound such as methanol, acetone and MEK, the trapping efficiency remains almost 100% over 20 minutes, which is enough for common applications.

For desorption, the trap is backflushed while being heated, and the trapped VOCs are easily desorbed from the microtrap. Figure 29 is a example of thermal desorption in multibed microtrap. In this test, a 5 ml of standard gas containing about 1 ppm organics was introduced to the multibed microtrap. Then thermal desorptions were made using different pulse times.

3.4 Summary

The microtrap is designed as an on-line preconcentrator and injection device for continuous monitoring of VOCs at trace level. The concentration of analyte and operating temperature significantly affect the breakthrough time and sampling flow rate has no effect on breakthrough volume. However, in the multibed microtrap system, ambient temperature variation did not affect the response and breakthrough time is enough long for most applications.

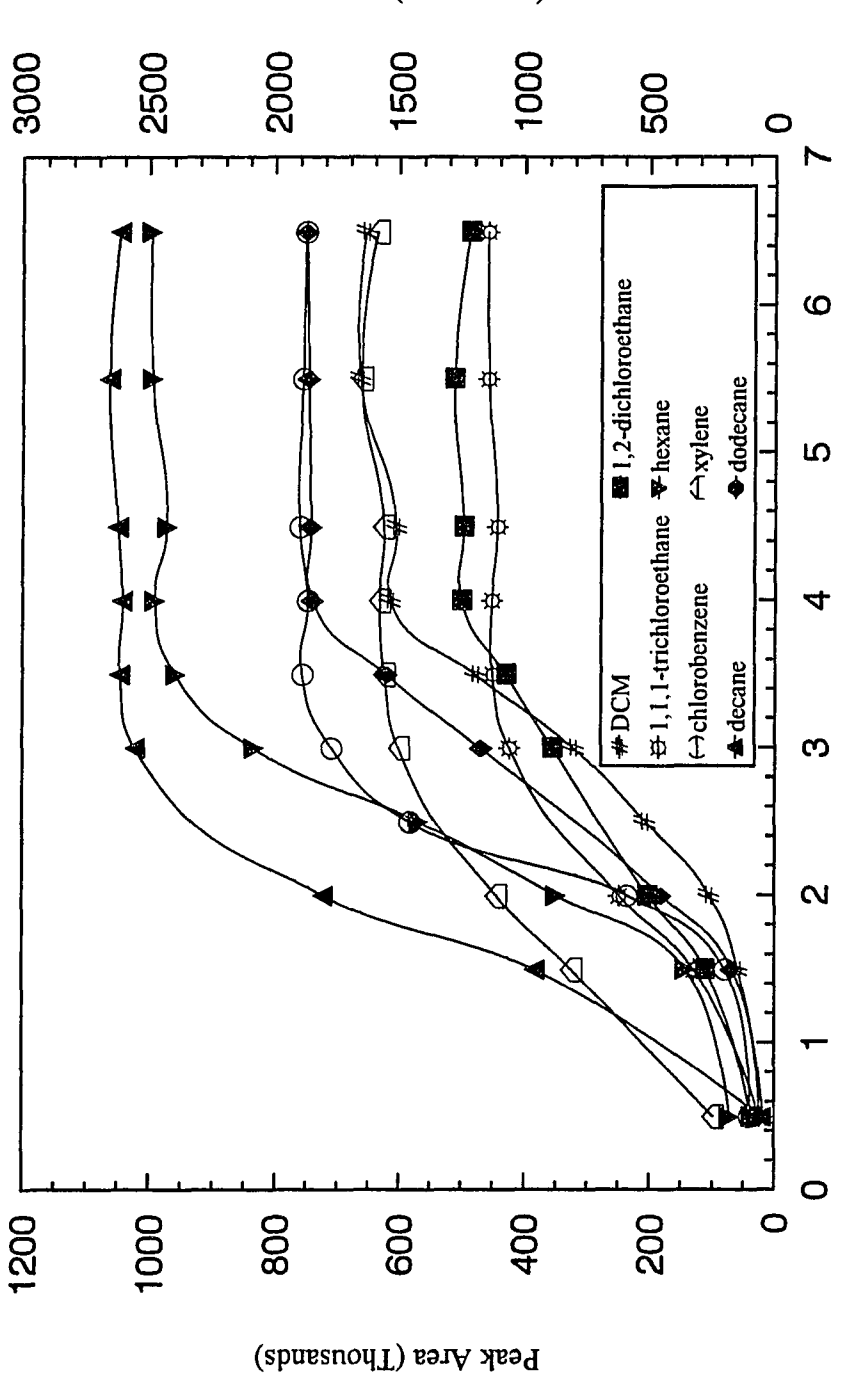


Figure 29 Effect of pulse time on desorption efficiency. A 6 inch long 0.74 mm id microtrap packed with Carbotrap C, Carbotrap (B) and Carbosieve S-III in series was used. The pulse current was 25 A.

CHAPTER 4

CONTINUOUS MONITORING OF VOLATILE ORGANIC COMPOUNDS IN AIR USING MICROTRAP BASED INJECTION SYSTEM

4.1 Background

As requirements for air pollutant regulation becomes more stringent, continuous monitoring methods which can track emissions from sources such as industrial stacks, vents etc. on a continuous basis are becoming more important. Continuous monitoring is also useful for keeping an emission inventory and for process control. Continuous 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, it can also save industry money in terms of resource conservation and recovery.

In general, spectroscopic techniques are ideal for process monitoring because of their analysis speed. For example, infrared (IR) methods are used in real time monitoring of compounds such as ammonia, hydrochloric acid, ozone, CO_2, NO_x and some organic compounds [11, 12]. However water vapor, which commonly exists in emission stream, can interfere seriously with regular IR analysis. A pretreatment for removal of water is required but prolongs the analysis time. Another problem is that it is difficult to identify individual organic compound in complex matrixes owing to the overlapping of absorbance bands from the different compounds [80]. Mass spectrometers have also been used for monitoring organic pollutants in gas emissions [13, 81]. They have some similar problems, such as the deconvolution of individual spectra in complex matrices and interference from H_2O, CO_2 etc. Moreover, both these techniques are quite expensive.

Gas chromatography (GC) is an excellent technique for separating organic compounds in complex samples. In general, chromatographic separation is much

slower than spectroscopic measurements. However, recent developments in GC have significantly reduced the separation time, which makes GC a viable real-time (or near real time) monitoring technique. A critical component of GC instrumentation for on-line monitoring is the sample introduction device, which has to make automatic injections at certain intervals. A multi-port sample valve is the most common injection device for process gas chromatography [24, 82]. However, this method has certain limitations in trace analysis. To obtain a large signal from a low concentration sample, a large injection volume is necessary. But a large injection requires a long injection time which causes band broadening, especially in capillary columns. Mostly, the injection volume is limited to several microliter to a milliliter which in turns raises the detection limit. Consequently, the sample valve is not adequate to face the challenge of trace analysis at the ppb levels. Furthermore, a sample valve intermittently injects a sample from the process stream and no information is available during the time period between two injections. This can be a serious limitations for monitoring processes which change with time, and in process control. Cryogenic traps have been used to concentrate the trace organic compounds in air analysis and may also be used in on-line process GC [83, 84]. However, the cryogenic traps are not suitable for samples with high humidity as moisture freezes in cryogenic trap. Cryogenic cooling is also a slow process which prolongs the analysis time.

Recently Mitra et. al. [30, 55, 57, 60] have reported the use of micro-sorbent trap for continuous on-line GC monitoring. It is a short length of narrow bore tubing which is packed with an adsorbent. It can be used to concentrate organics and is then rapidly heated to desorb the organics as a concentration pulse which acts as a GC injection. It can be used as a stand-alone device or in conjunction with a gas sampling valve. It can be attached directly in front of the GC column in place of a sampling valve and it is referred to as an on-line

microtrap (OLMT). When the gaseous sample stream is passed through the OLMT, the organic analytes of interest are trapped in the microtrap. Then the adsorbed analytes can be thermally desorbed by electrical heating. Because the microtrap has a low heat capacity, rapid heating is possible to desorb the organics as a narrow injection band. Continuous monitoring is done by heating the microtrap at regular intervals and, corresponding to each pulse, a chromatogram is obtained. The microtrap accumulates the organic analytes during the interval between pulses (pulse interval). So it serves as an injector as well as a preconcentrator and exhibits a high sensitivity and low detection limits. However, in the OLMT system, the sample matrix gas is used as a part or whole of the carrier gas. Thus oxygen and moisture in the sample are directly introduced into GC column and detector, which may deteriorate the delicate GC column.

The sequential valve microtrap (SVM) has also been reported recently as a injection device for continuous monitoring [31]. In this technique, a microtrap is connected in series with a gas sampling valve. A large volume injection (several milliliters) or several small volume injections are made by the sample valve. The analytes are trapped by the microtrap. Then the microtrap is electrically heated to desorb the analytes as an injection for the GC separation. The SVM configuration has an advantage that the microtrap can be isolated from the process stream when not in use. However, SVM has the low sensitivity compared to OLMT over the same cycle time. No information about the stream can be obtained between two injections since a sampling valve is used in the SVM. Moreover, much sample matrix gas is still introduced into GC column.

In this research, a new microtrap based injection system, the on-line microtrap-backflushing (OLMT-BF) system, was developed and investigated. In the OLMT-BF system, a microtrap replaces the sample loop of a valve. When the sample valve is in the loading mode, the sample stream continuously flows through

the microtrap and the analytes are retained by the microtrap. In the injection mode of the valve, carrier gas flows through the microtrap and at that moment a pulse heating is applied to the microtrap. Thus, the carrier gas strips the desorbed analytes into GC column. Comparison among valve, SVM and OLMT-BF has been made. Some data from monitoring of real air samples from a smog chamber are presented.

4.2 Experimental

4.2.1 Reagent and Materials

The organic chemicals were chromatographic grade from Fisher Scientific. Adsorbents such as Carbotrap™ C came from Supelco Company (Bellefonte, PA). Gas samples were prepared in 6-L evacuated canisters by injecting pure liquid organic solvent and filling with dry zero air to 40 psi pressure. The gas samples were verified by comparison with a standard gas mixture from AIRLIQUIDE Inc. (Morrisville, PA). The simulated incineration gas from AIRLIQUIDE contains 1 ppm of benzene, trichloroethane, toluene, ethyl benzene; 9.27% of CO_2, 10.9% of O_2, 164 ppm sulfur dioxide, 75 ppm carbon monoxide and balance nitrogen.

4.2.2 Instrumentation

A schematic diagram of the continuous monitoring system used in this study is presented in Figure 30. The gas sample valve was a six-port air actuated valve with a digital interface (Valco Instruments Co. Inc., College Station, Texas). The operating modes of valve were controlled by a computer. The microtrap was made by packing a 0.53 mm i.d. silica lined stainless steel tubing (Restek Co., Bellefonte, PA) with 60 mesh Carbotrap™ C. The microtrap was connected to a variable power supply (20-50 V AC). A computer controlled electric switch was used to control the interval between pulses and also the pulse time for which the

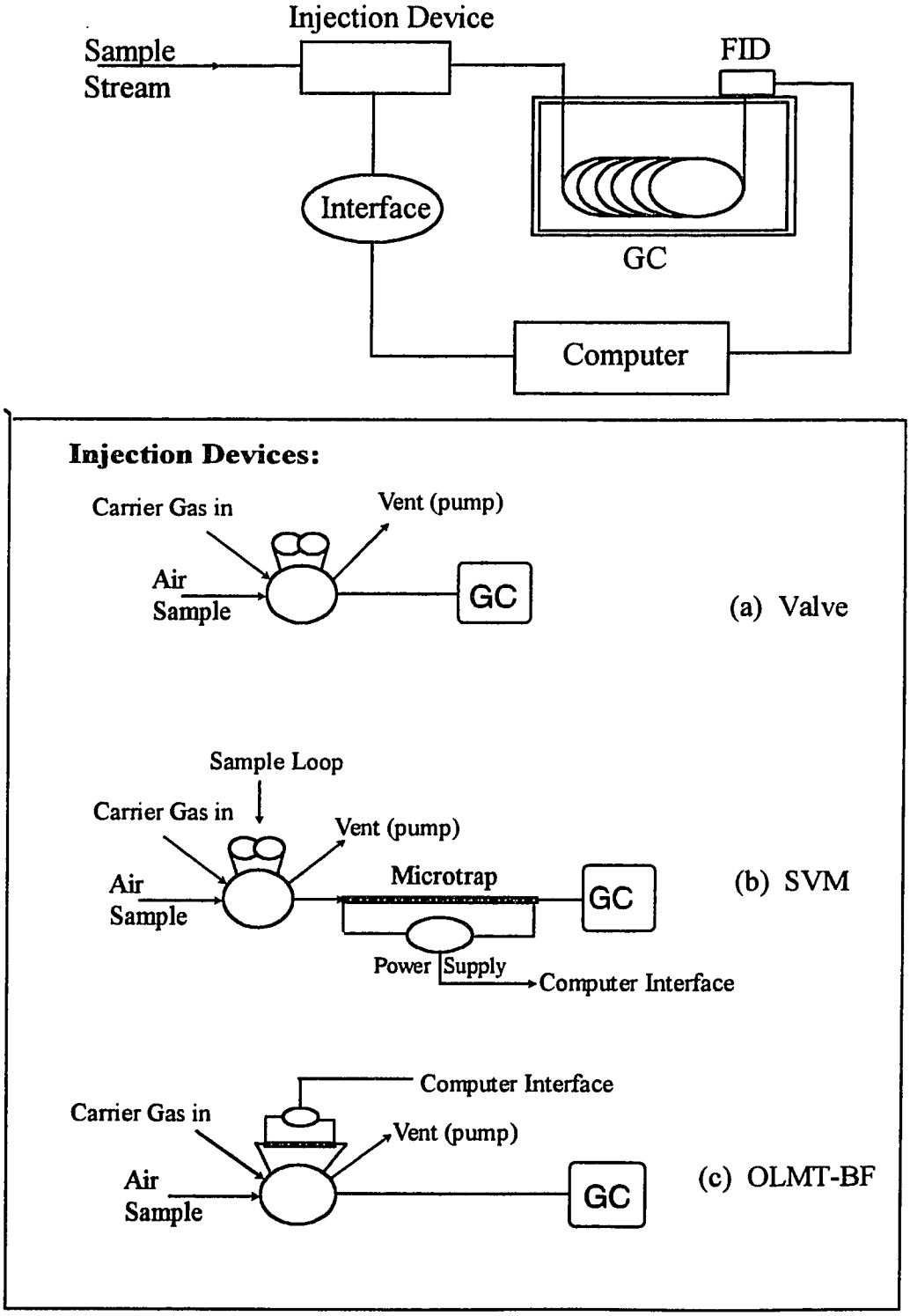


Figure 30 Continuous monitoring system showing the different injection systems.

microtrap current was turned on. Power resistors were put in series with the microtrap to limit the current through it. Details on the microtrap and its operation are presented elsewhere [30].

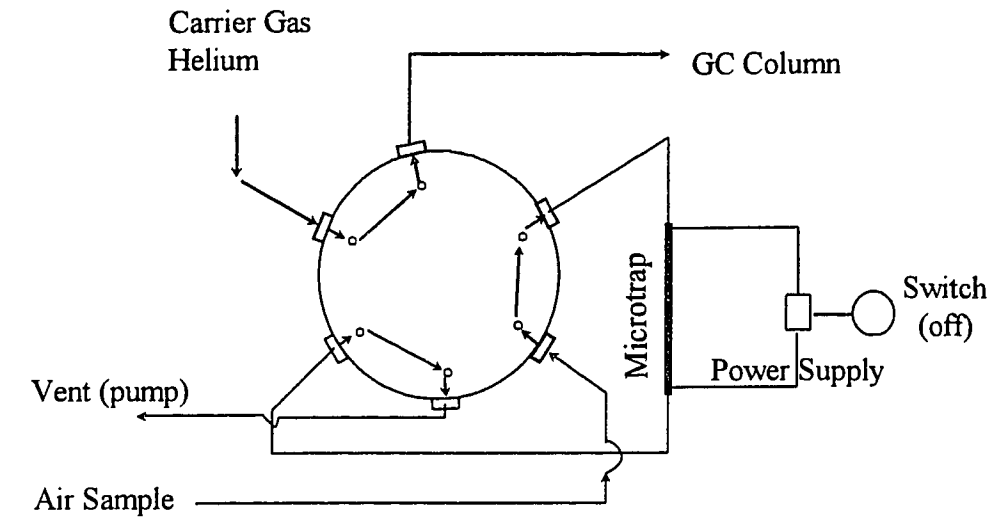
A Hewlett Packard 5890 Series II gas chromatograph (Hewlett Packard Company, Avondale, PA) equipped with a conventional flame ionization detector (FID) was used for this study. A 30 m long DB-624 fused silica open tubular column from J&W Scientific Inc. (Folsom, CA) was used. The column inner diameter was 0.53 mm, and the stationary phase thickness was 3.0 micron. Nitrogen was used as the carrier gas and flow rates were between 5 to 7 ml/min.

4.3.3 OLMT-BF System

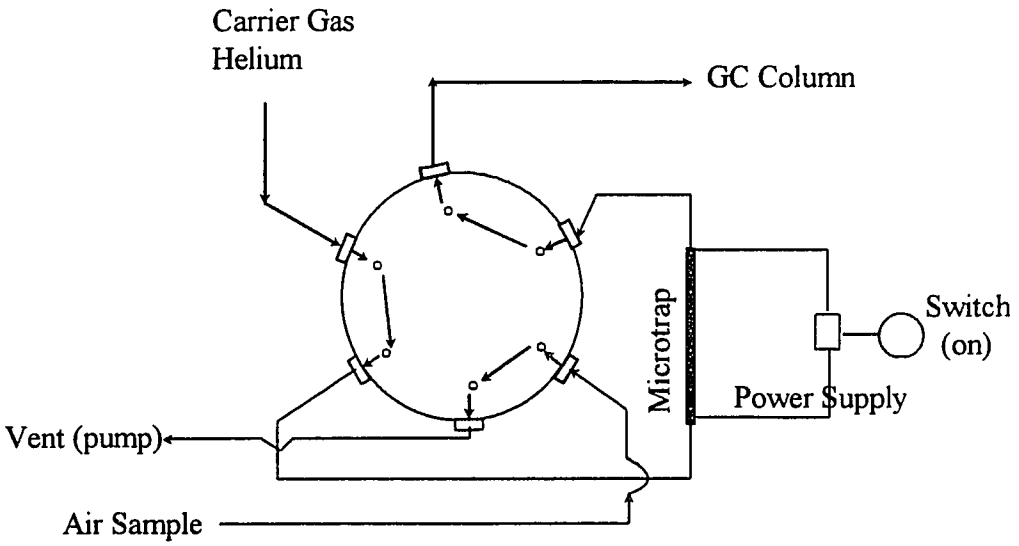
A microtrap replaces the sample loop in a sampling valve. When the sampling valve is in the loading mode, the sample continuously flows through the microtrap and is vented. The analytes are trapped by the microtrap. In the injection mode of valve, carrier gas flows through the microtrap and into the GC column. At that moment a heating pulse is applied to the microtrap. Thus carrier gas strips the desorbed analytes into GC column as an injection. The operation modes are presented in Figure 31.

4.3.4 Continuous Monitoring of Reaction in A Smog Chamber

In real sample monitoring experiments, selected aromatic organic compounds, propene and NO_x were injected into two 20 m^3 smog chambers (Atmospheric Chemistry & Aerosol Lab, California Instate of technology, Pasadena, CA). The detailed smog chamber experiments have been described elsewhere [85, 86]. The initial concentrations of organic compounds were around 500 ppb. The smog chambers are exposed to sunlight to start the photochemical reaction. A



(A) Loading Mode



(B) Injection Mode

Figure 31 The Operation modes of OLMT-BF system.

sequential valve microtrap system was used as an injection device and preconcentrator for on-line monitoring of the organic compounds in the gas phase. The experimental diagram is presented in Figure 32. Every 15 minutes an injection was made into the GC. The switching valve was used to switch the sample stream from Chamber A and Chamber B. The filter was used to remove particles from the gas sample.

4.3 Results and Discussion

The three injection devices (valve, SVM, and OLMT-BF) were tested using simulated stack gas standard. The gas contained 1 ppm each of benzene, toluene, ethyl benzene and trichloroethane along with combustion products such as CO_2 (9.27%), CO (75 ppm), SO_2 (164 ppm) and O_2 (10.9 %) etc. In each case, the gas stream flowed continuously through the injection device and an injection was made every two minutes. A chromatogram containing the four peaks was obtained every time an injection was made. The chromatogram is presented in Figure 33.

As expected, the valve with a 100 μl sample loop showed a relatively small response compared to the SVM, and the OLMT-BF system (Figure 33a). When the volume of the sample in the valve was increased to 8 ml, broad overlapping peaks were obtained as in Figure 33b. In the SVM mode, when microtrap is connected in series with the 8 ml sample loop, then the analytes are refocused and injected into the GC, generating sharp peaks as shown in Figure 33c. The OLMT-BF system generates even larger signals than the SVM (Figure 33d). In this case the sample flows continuously through the microtrap and effectively concentrates all the analytes. The effective sample volumes analyzed by the valve, SVM and OLMT-BF in this Figure are 100 μl, 8 ml, and 19.2 ml, respectively. In Figure 33, for the same sample OLMT-BF generated the largest signal followed by SVM and then

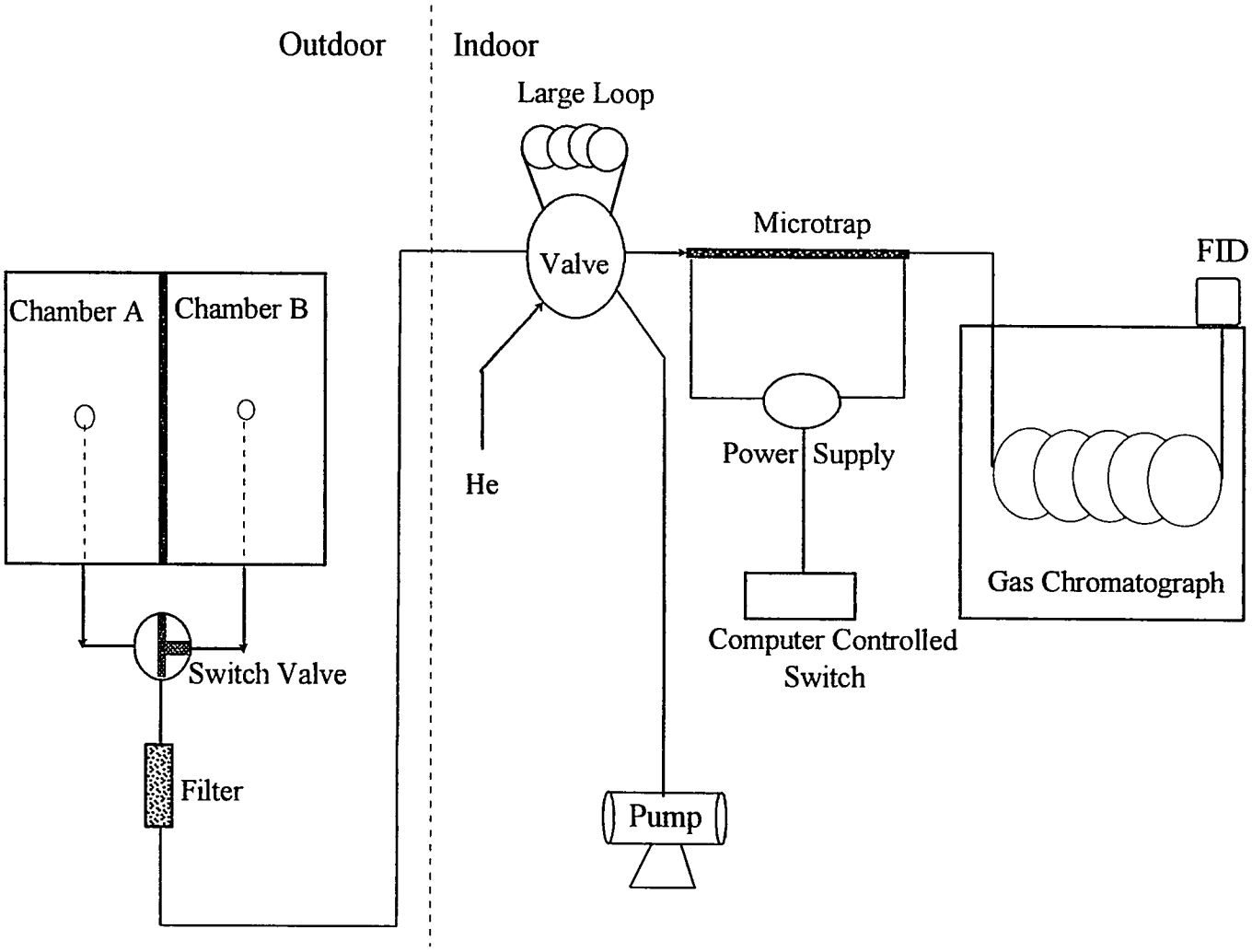


Figure 32 On-line monitoring of VOCs in the smog chambers using SVM system.

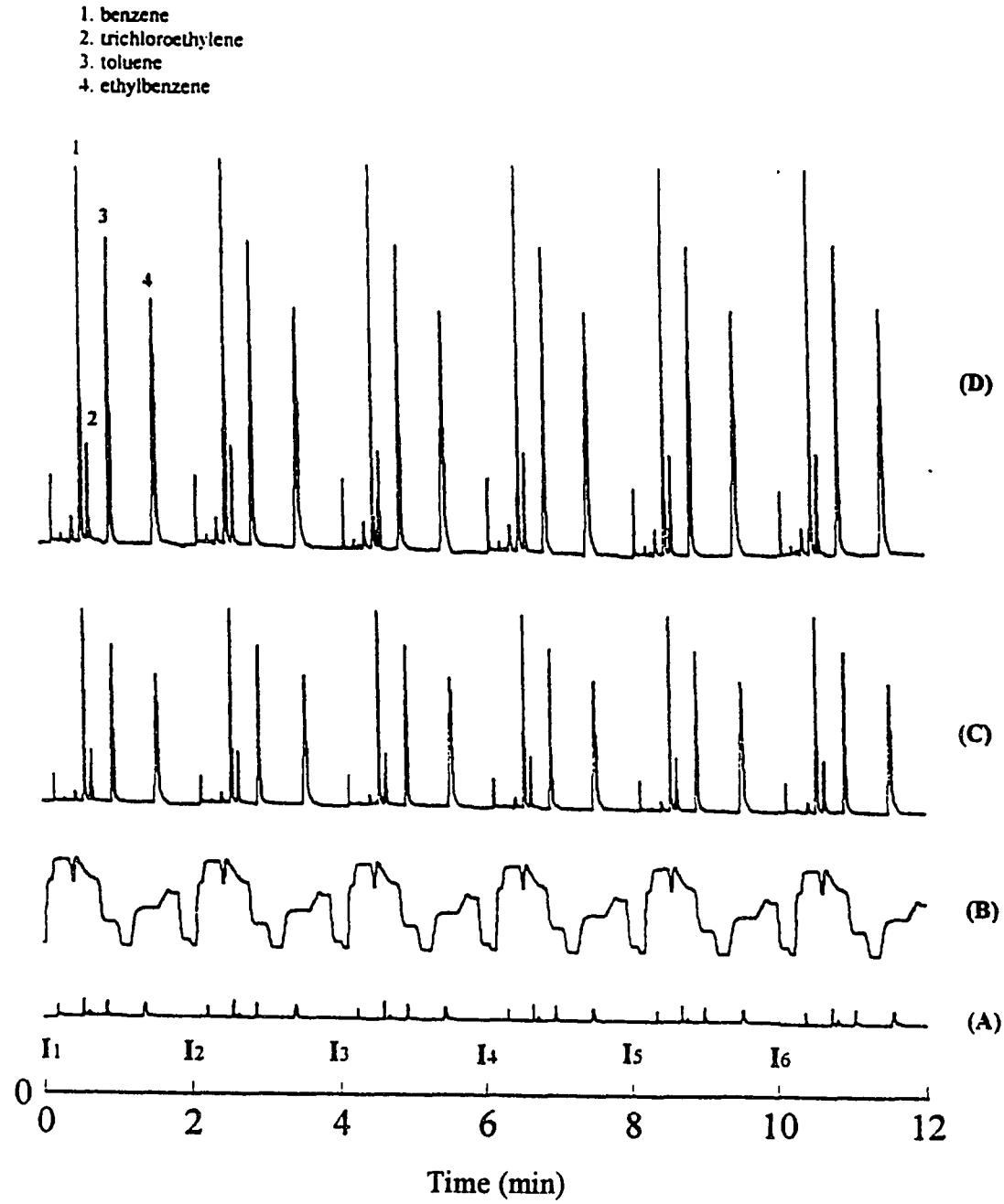


Figure 33 Continuous monitoring of VOCs in a simulated stack gas containing combustion products along with volatile organic compounds. In each case injections were made every 2 minutes at points I_1, I_2...: (A) response using a 100 μl gas sampling valve; (B) response from an 8 ml sample loop; (C) response using the SVM mode (the volume of sample loop was 8 ml); (D) response from OLMT-BF mode.

the conventional sample valve. Thus the OLMT-BF has similar high sensitivity to the OLMT. Furthermore, the OLMT-BF has some advantages over the OLMT. The OLMT-BF isolates the GC detection system from the sample stream and no sample matrix gas is introduced into GC column. A pressurized sample is not necessary in the OLMT-BF and the OLMT-BF system can easily take the sample from the stream by connecting a vacuum pump to the vent port in the valve. Moreover, in the OLMT-BF system, backflushing desorption can be used to improve the desorption efficiency, especially for a multibed microtrap.

4.3.1 Response Characteristics of SVM and OLMT-BF

Most process or emission streams change with time and the goal of on-line measurement is to monitor these changes. Sometimes the variation can be very rapid. The changes may occur for a few minutes or even a few seconds. In chromatography, the separation time may be of the order of several minutes. Conventional gas sampling valves inject the sample every a few minutes from the process stream. No information about the process stream can be obtained during the period between two injections. On the other hand in the OLMT and OLMT-BF, the sample continuously flows through the microtrap and the microtrap acts as a sample accumulator. Eventually when the trap is heated, a signal proportional to the amount of accumulated sample is obtained. So, indirectly, we do get information about the time period between the pulses. Here we test the response of all the three injection devices to impulses of various frequency.

Figure 34A is a profile of the hexane concentration in a simulated process stream. Within 30 minutes, there were three concentration spikes of hexane added to the gas stream: the first spike occurred after 2.5 minute and finished within 10 seconds, the second spike occurred at 4.5 minute and lasted for 1.2 minutes, and the third spike occurred at 10 minute and lasted for about 12 minutes. The results

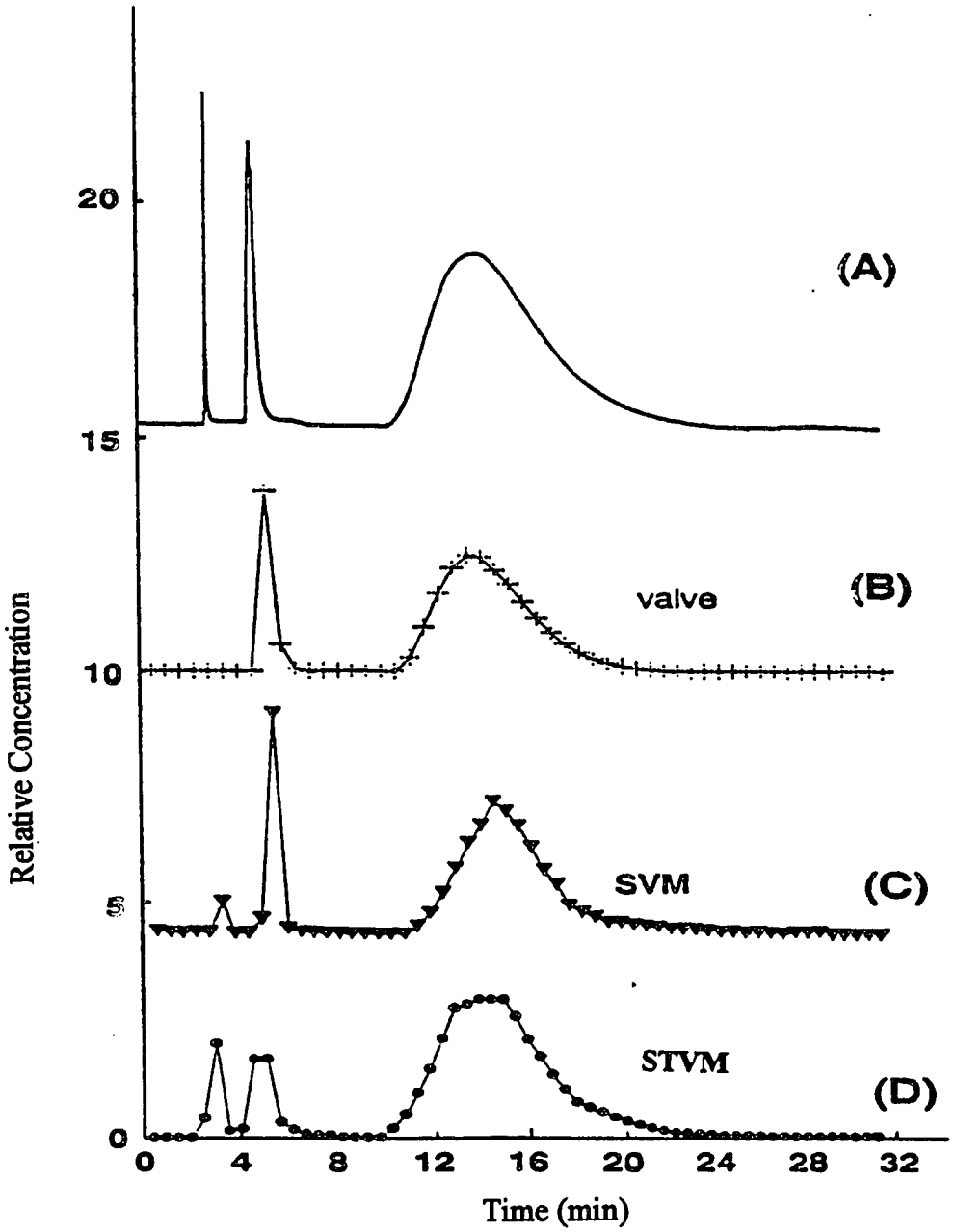


Figure 34 Response of the different injection system to a changing concenration stream: A) concentration profile of the inlet stream; B) monitoring using a gas sampling valve; C) monitoring in the SVM mode (three valve injections followed by a microtrap pulse); D) monitoring in the OLMT-BF mode. In each case injections were made every 30 seconds.

of monitoring hexane in this synthetic gas stream are presented in Figure 34 B, C, D using the three injection techniques. In each case injections were made every 30 seconds. It can be seen that first spike was missed by the valve. The only way the valve can detect this spike is when an injection occurs during the duration of the concentration spike. The probability of such an occurring is low since the spike only lasted for 10 second. We repeated this experiment 20 times and only twice were the positive results. In the SVM operation here, multiple small injections by 100 μl sample valve were followed a microtrap pulse. The valve requires 5 seconds for both loading and injection. Three injections were followed by a heating pulse. SVM may also miss the first peak while it uses a common valve for sampling and the probability of positive results is 75%. The OLMT-BF system can track the sample stream all the time since the sample continuously passes through the microtrap and the heating/cooling cycle only takes 2-3 seconds. In each of twenty replicates, the 10 second peak was detected. This clearly demonstrated the effectiveness of the microtrap based injection systems in monitoring streams which may change rapidly with time.

4.3.2 Calibration Curve and Detection Limits

Linearity of the calibration curve is a crucial consideration for continuous quantitative analysis. The amount of analyte trapped by the microtrap is theoretically proportional to the concentration of sample through it. The calibration curves for these three techniques are presented in Figure 35. Again we can see that at the same concentration, the response of OLMT-BF system is much larger than that of the valve or the sequential valve microtrap. The lowest detection limits are obtained using the OLMT-BF system. The detection limits for some VOCs are presented in Table 6.

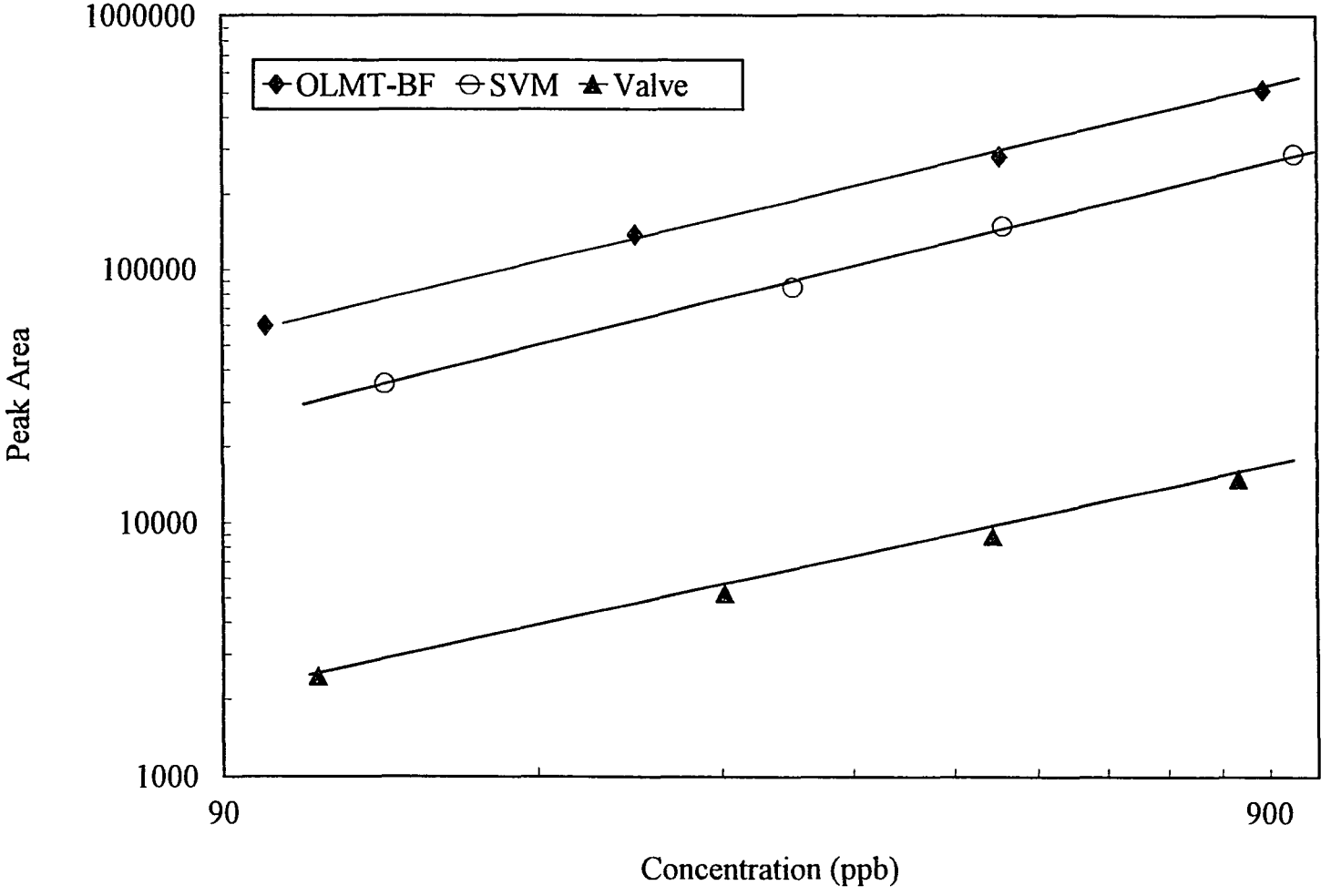


Figure 35 Calibration curves using the three injection devices.

Table 6 Detection Limits for Some Typical VOCs

Compounds	detection limits (ppb_V) [a]		
	Valve [b]	SVM [c]	OLMT-BF [d]
benzene	23.6	0.28	0.15
toluene	8.35	0.092	0.045
m-xylene	7.55	0.048	0.026

a. The detection limits were calculated by ratio of signal to noise at 3.
b. The volume of sample loop is 100 μl.
c. The volume of sample loop is 8.0 ml and the sequential valve microtrap was operated by one valve injection following one microtrap pulse. The temperature of microtrap was 28°C.
d. Flow rate of sample stream was 5.6 ml/min and interval between two microtrap pulses is 3 minutes. The temperature of microtrap was 28°C.

4.3.3 Retention Mechanism of The Microtrap

The microtrap is made from capillary tubing so that it has low heat capacity and can be heated very quickly to generate a sharp injection. Consequently, it contains a small quantity of adsorbent which can retain the analytes for a limited amount of time before breakthrough occurs. The microtrap is equivalent to a short GC column. When a pulse injection of sample is introduced to the microtrap, the retention time (t_R) depends upon its capacity factor [30]:

$$t_R = (k + 1)b/\mu \qquad (4.1)$$

where k is the capacity factor of analyte in the microtrap; b is the length of microtrap and μ is the linear velocity of the carrier gas. Breakthrough time can be defined as the time at which 99% analyte is trapped in the microtrap. So the breakthrough time is different from retention time and always is less than retention time. However, the breakthrough time is close to the retention time when the theoretical plate number of trap is larger than 120. In this case the theoretical

number of plates for the microtrap was estimated to be 150. Thus the breakthrough time (t_b) can be assumed to be close to retention time (t_R).

According to equation (4.1), the breakthrough time increases with the capacity factor of analytes for a fixed length of microtrap, and constant linear velocity of carrier gas. The larger the capacity factor of analyte, the longer is the breakthrough time. The capacity factor, of course, depends upon analyte-adsorbent interactions. For a given adsorbent the capacity factor depends upon the analyte and microtrap temperature. Figure 36 presents a elution profile of several typical analytes in the microtrap. It was obviously observed that toluene was retained by the microtrap about 23 minutes but ethanol was only retained 15 seconds since the breakthrough volume of toluene (6.50×10^5 ml/g at 20°C) is much larger than that of ethanol (4.93×10^2 ml/g at 20°C) [87]. Trapping efficiency as a function of time is presented in Figure 37. The trapping efficiency of acetone decreases rapidly since acetone has a short breakthrough time. For toluene, which has high capacity factor and long breakthrough time, the trapping efficiency stays at 100% for about 23 minutes before dropping slowly. The advantage of high capacity factor is two fold. First, the sample is retained for a long time, and second, the emerging band is broad so that even if the trap is heated during the elution of the analyte band, at least part of the sample can be desorbed for analysis. For example, in case of toluene it takes almost 10 minutes for trapping efficiency to decrease from 100% to 0%.

The breakthrough time also decreases with linear velocity of the carrier gas. Figure 38 shows the effect of the linear velocity on t_b at different temperature. A linear relationship between t_b and $1/\mu$ was obtained at different temperature. For a given adsorbent and microtrap, the capacity factor for a certain analyte is a function of temperature. An empirical equation of the following form has been suggested [88, 89]:

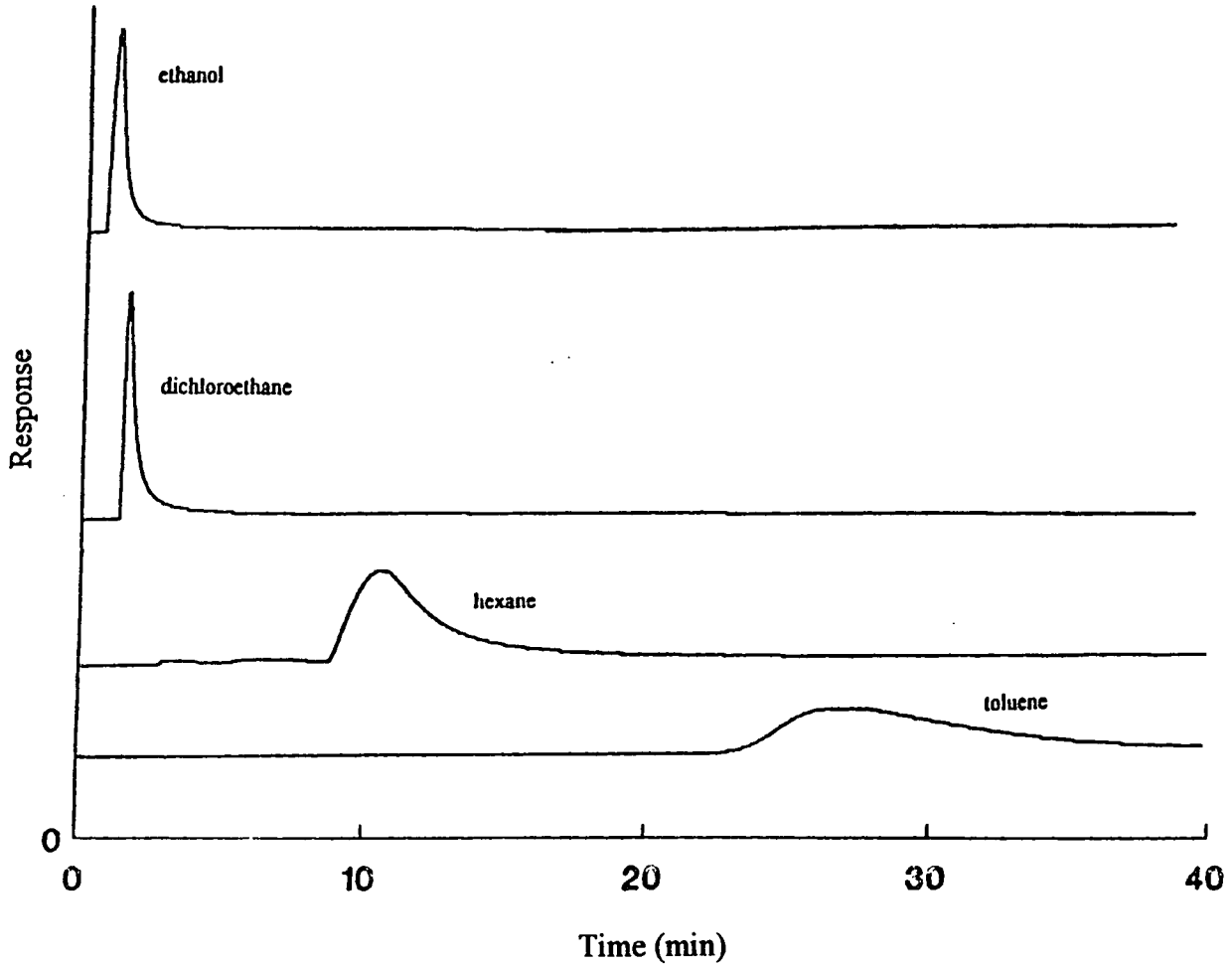


Figure 36 Elution profiles of different organic compounds in a 9 inch long microtrap. Microtrap temperature was 30 °C and the flow rate of carrier gas was 6 ml/min.

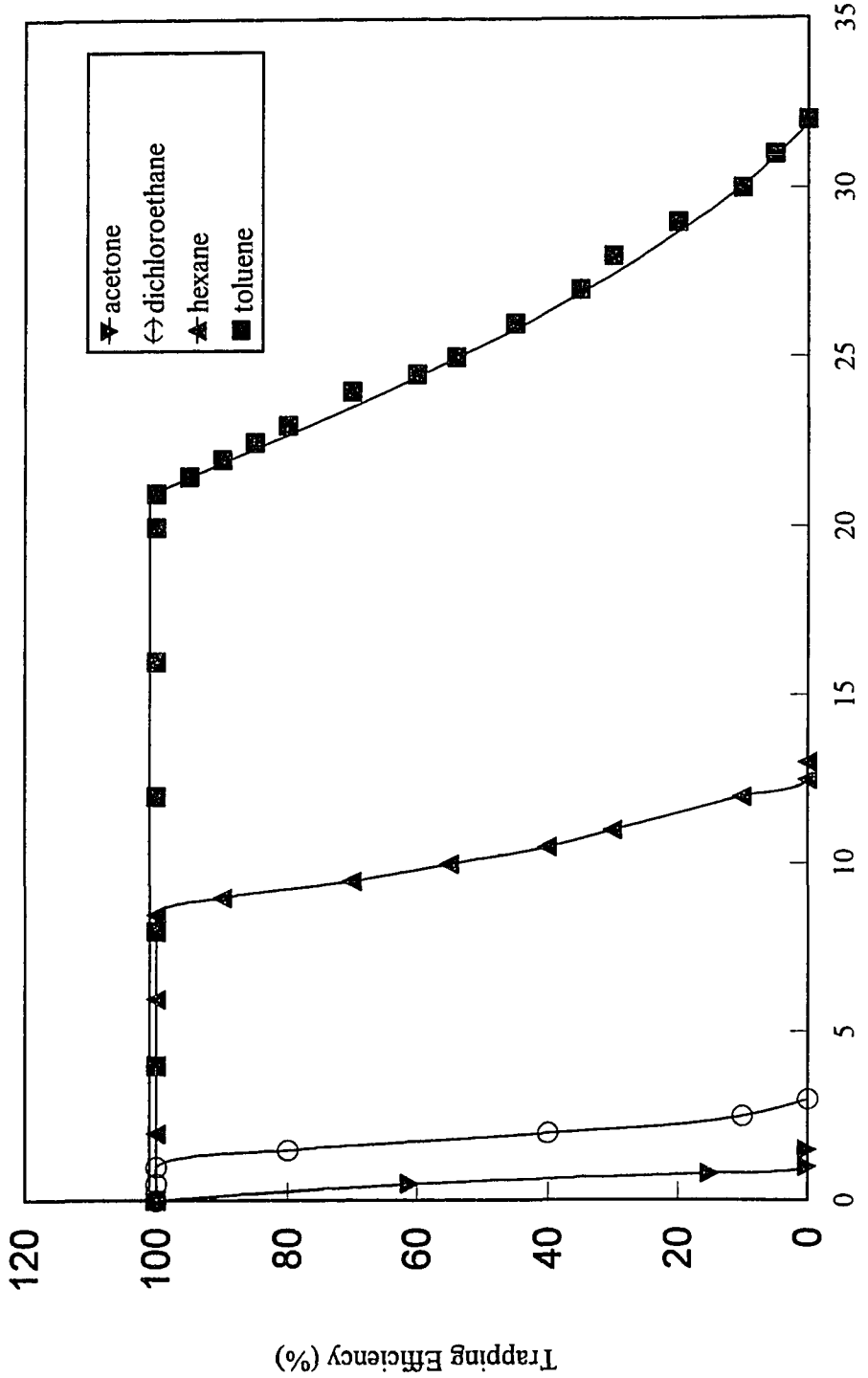


Figure 37 Trapping efficiency of a microtrap as a function of delay time. A 9 inch long 0.53 mm i.d. microtrap packed with Carbotrap C was used. The microtrap temperature was 303 K.

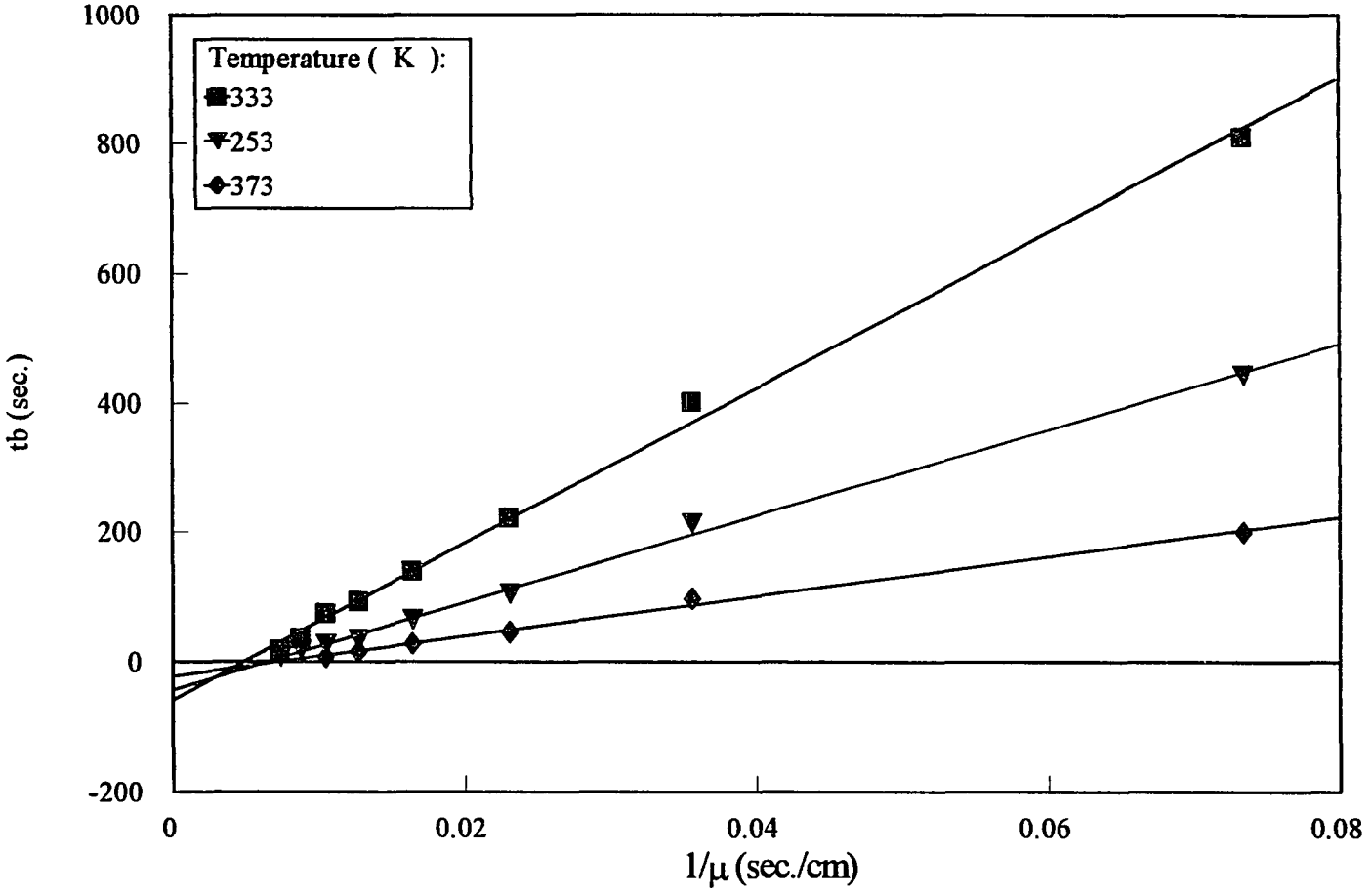


Figure 38 Effect of linear velocity on breakthrough time. A 9 inch long 0.53 mm i.d. microtrap packed with Carbotrap C was used. The GC injection method was used for the determination of t_b.

$$k = k_0 \exp.(-\Delta H/RT) \qquad (4.2)$$

here k_0 is the capacity factor at reference temperature; ΔH is an absorbing energy; R is a constant and T is the temperature of microtrap. When temperature increases the capacity factor decreases so that breakthrough occurs more quickly. If equation (4.2) is used to replace k in the equation (4.1), t_b as a function of temperature can be expressed as:

$$t_b = (1 + k_0 \exp.(-\Delta H / RT)) \frac{b}{\mu} \qquad (4.3)$$

The adsorbents are always chosen so that capacity factor is relatively high and significantly higher than one, thus equation (4.3) is approximated as:

$$\ln t_b = \frac{C}{T} \qquad (4.4)$$

where C is a constant at fixed microtrap length and linear velocity of carrier gas. As expected from equation (4.4), a straight line was obtained when $\ln(t_b)$ and 1/T were plotted against one another (Figure 39). It is obvious that the breakthrough time decreases rapidly with increasing microtrap operation temperature. For practical reasons, it may be advantageous to design a microtrap to operate near room temperature. Subambient operation requires cryogenic or other elaborate cooling devices, while higher temperature reduces t_b.

For a continuously flowing sample, if breakthrough occurs, the trapping efficiency of the microtrap decreases. As a result, the system response and sensitivity are reduced. For example, the results in Figure 40 show that the response of dichloromethane decreased with increased operating temperature. The interval between consecutive pulses in this experiment was one minute which is larger than the breakthrough time of dichloromethane (30 seconds at 30°C). As the microtrap temperature was increased, the breakthrough time became shorter; more analyte broke through, reducing the trapping efficiency and the system response. However, the responses for toluene and ethylbenzene stayed constant in the lower

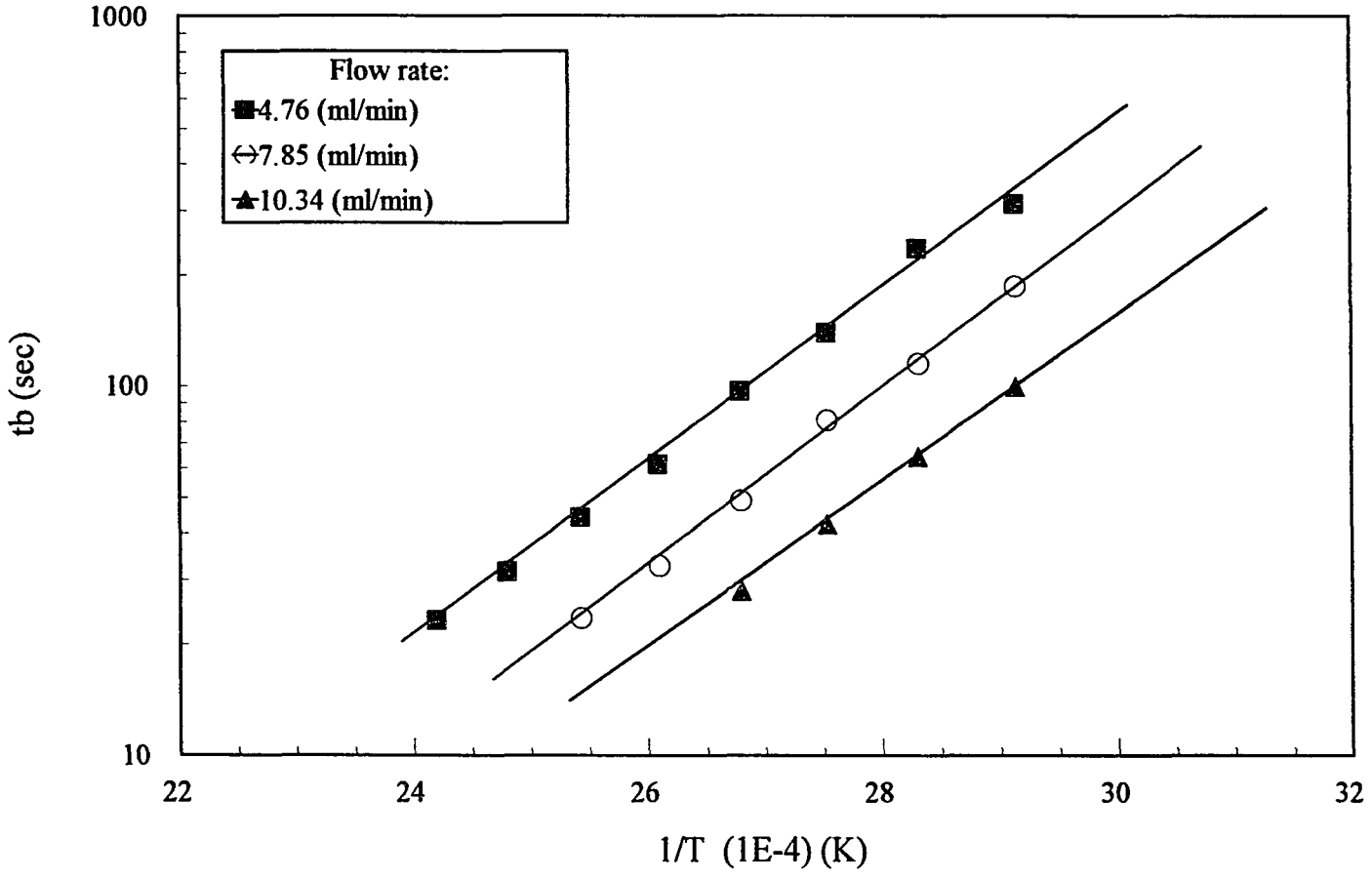


Figure 39 Effect of microtrap temperature on breakthrough time (t_b). A 9 inch long 0.53 mm i.d. microtrap packed with Carbotrap C was used. A GC injection method was used to determine the breakthrough time.

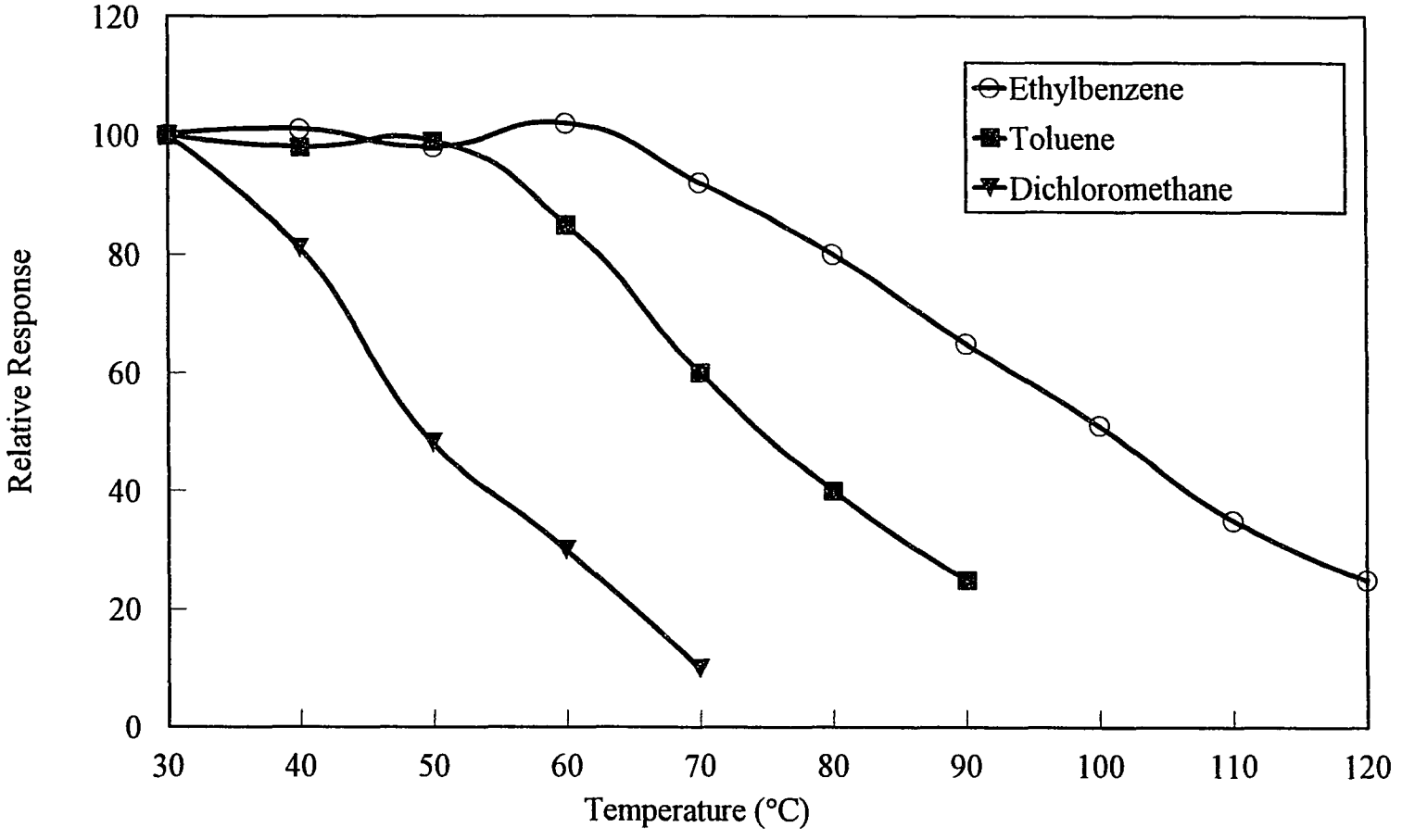


Figure 40 Effect of operation temperature of microtrap on relative response. A 9 inch long 0.53 mm i.d. microtrap packed with Carbotrap C was used. The standard gas contains 1 ppm of tested compounds. The pulse interval was 1 minute and the flow rate was 5 ml/min.

temperature region because t_b remained larger than 60 seconds. For ethyl benzene there was no change when microtrap temperature was in the range of 30 to 60 °C. When the temperature was increased further, breakthrough began to occur and response began to decrease. The flat region in Figure 36 is a good operating region, because small fluctuations in microtrap temperature do not effect system response.

In general, in considering reduction in sensitivity due to sample breakthrough, the pulse interval needs to be considered along with temperature. For example, in Figure 41 it can be seen that the constant region in the trapping efficiency vs. temperature curve decreases with the pulse interval. Basically, at lower operating temperature, the microtrap shows high sensitivity and low detection limits for volatile organic compounds. However, for the compounds which have long breakthrough times, the detection limits can not be decreased by lowering the operating temperature.

4.3.4 On-line Monitoring of Organic Compounds from Smog Chambers

The SVM system was tested in smog chamber studies at the Aerosol & Atmospheric Chemistry Lab, California Institute of Technology. The goal of these studies was to study the mechanisms of photochemical reactions and aerosol formation of aromatic hydrocarbons in atmosphere. The smog chambers were 20 m^3 in size. Two side by side chambers were spiked with 500 ppb of toluene and m-xylene, respectively. Propene and NO_x were also added to both sides as reaction initiators. Then the smog chamber was exposed to sunlight and allowed to react. The air samples from chamber A and B were alternately passed through the sequential valve microtrap by a switch valve. The particles in gas phase were removed by an aerosol filter. The sampling flow rate was about 50 ml/min. Every 15 minutes, one injection was made into the GC using a 8 ml sample loop. The

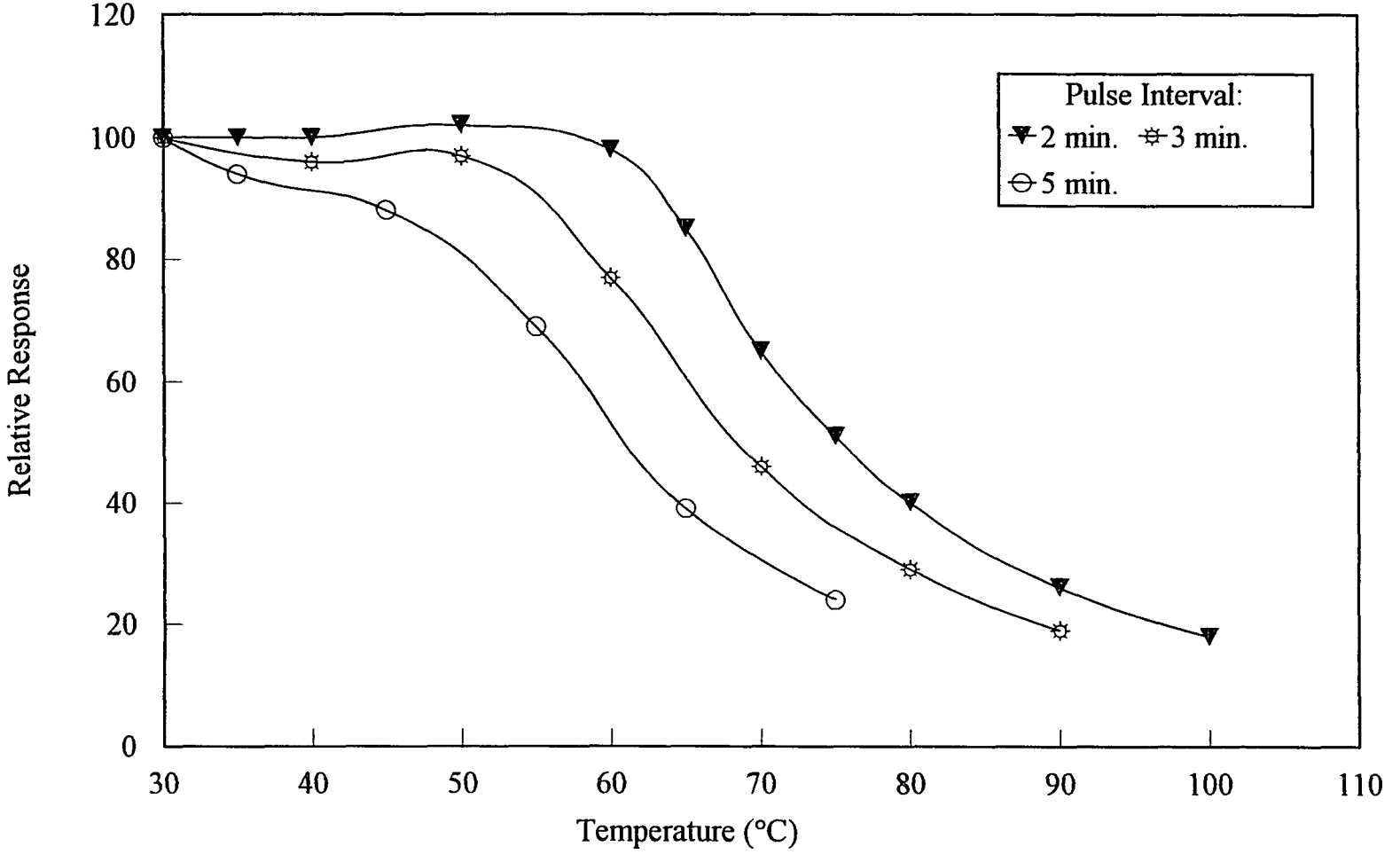


Figure 41 Effect of microtrap temperature on relative response at different pulse intervals. A 9 inch long 0.53 mm i.d. microtrap packed with Carbotrap C was used. The standard gas contains 1 ppm of ethylbenzene. The pulse interval was 1 minute and the flow rate was 5 ml/min.

decay profiles of toluene and m-xylene are shown in Figure 42. Under same conditions, the decay rate of m-xylene is much faster than that of toluene. These photochemical reactions are relatively slow and the concentrations were not very low. Consequently, this study did not fully challenge our system. Still this study demonstrated the effectiveness of the SVM system. The SVM system was preferred over the OLMT-BF here for two reasons: first we were dealing with relatively higher concentrations and, secondly, switching between Chamber A and B was easy with the SVM.

4.4 Summary

The microtrap based injection has shown some advantages over the valve as injection device in continuous monitoring system for VOCs. The OLMT-BF system has a higher sensitivity and a lower detection limit. The SVM and OLMT-BF systems can track VOCs in the sample stream all the time, while valve injections can miss concentration spikes. The OLMT-BF has some advantages over the OLMT such as the isolation of GC system from the sample stream, avoidance of the sample matrix gas entering the GC column, and suitability for backflushing desorption. Real sample tests carried out on real samples in monitoring the air from a smog chamber demonstrated that the microtrap based injection device is reliable, reproducible and is appropriate for continuous monitoring of VOCs at ppb levels.

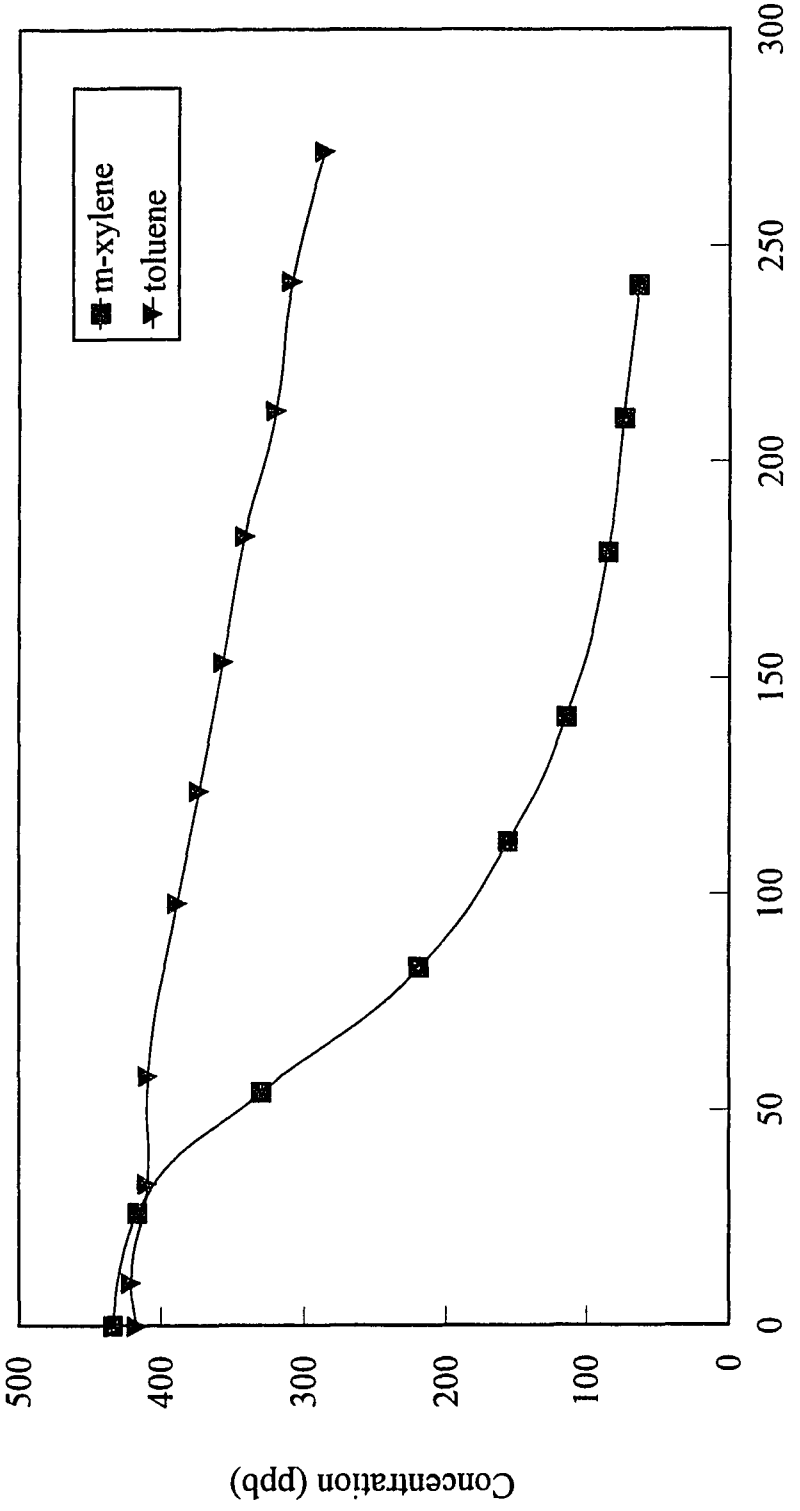


Figure 42 Decay profile of initial compounds in the smog chamber. A SVM system was used to monitor the aromatic compounds in the smog chambers. The microtrap was 9 inch long, 0.53 mm i.d. and packed with Carbotrap C.

CHAPTER 5

CONTINUOUS MONITORING OF VOLATILE ORGANIC COMPOUNDS IN WATER USING ON-LINE MEMBRANE EXTRACTION AND MICROTRAP GC SYSTEM

5.1 Background

The list of volatile organic compounds (VOCs) includes a variety of alkyl substituted aromatic hydrocarbons, as well as organic molecules containing different functional groups. Presence of VOCs in water is a public health concern because many of the VOCs are toxic and/or carcinogenic. VOC contamination may be encountered in ground water, surface water, and industrial waste water as well as in drinking water. VOCs may come from industrial spills and emissions, leachate from municipal and industrial landfills, and can be formed as byproducts of chlorination during the water treatment process. Federal regulations require monitoring of effluent streams for the presence of VOCs.

The conventional, Environmental Protection Agency (EPA) approved, method of collection and analysis of VOCs in water consists of obtaining a grab sample, transporting the sample to a laboratory and analyzing the sample by purge and trap (e.g., EPA 502.2, 602 methods). In purge and trap, the VOCs are purged from the aqueous sample by bubbling an inert gas through it. The inert gas carries the VOCs into a sorbent trap where they are retained. Then the VOCs are thermally desorbed from the trap and analysis is done by GC or GC/MS. Head space analysis is another popular method, where the sample is first allowed to equilibrate in a sealed sample vial. Then a small head space sample is withdrawn and analyzed by GC or GC/MS. There are several inherent difficulties in the purge and trap procedure, such as memory effects and incomplete desorption. The head space analysis has relatively poor accuracy and precision, and is usually used as a screening method. Direct injections of water samples have also been tried for analysis of VOCs, but the detection limits are usually quite high [90].

The limitation of the above mentioned techniques is that the sample has to be sent to the laboratory for analysis. These techniques can not be used for real-time, continuous monitoring. Real-time, on-line monitoring of VOCs in water offers several advantages. On-line techniques provide a more accurate analysis of VOCs by eliminating the problems associated with discrete sampling, sample preservation, transport, storage and laboratory handling of samples. Each of these steps may introduce errors such as sample loss and cross contamination. The grab samples are usually stable for a few days and the analysis has to be done within a few days. Very often samples have to be rejected just because the analysis could not be completed on time. Some of these problem can be solved using on-line monitoring techniques. Real-time VOC measurement devices can be used for continuous monitoring applications, such as, monitoring ground water during clean up operations, drinking water supply, and waste water discharge from industries. Continuous monitoring can also be used in process control applications. Semicontinuous VOCs monitoring systems for water have been developed based on purging of VOCs from water followed by IR or GC analysis [12]. At present there is a real need for a continuous monitoring technique which can separate and identify the different VOC components at trace level.

5.1.1 Membrane Extraction of VOCs

In general, VOCs analysis in water involves an extraction separation step where the VOCs are removed from the aqueous phase. The most common extraction method is purging with an inert gas as done in purge and trap. However, purging is a slow process and significantly increases the analysis time. The VOCs can be recovered from the aqueous phase via selective transport through a semi-

permeable membrane. In this process, the aqueous sample is contacted with a membrane and the VOCs selectively permeate through the membrane into a gaseous phase on the other side. Membranes can be divided into two categories: nonporous and porous membranes. In nonporous membranes, the mechanism of VOCs permeation [91] involves the following steps. First the VOC components migrate from the aqueous phase to the surface of the membrane, and dissolve in the inside surface layer of membrane. Then the dissolved components migrate through the bulk membrane under a concentration gradient. This is followed by evaporation or stripping of the VOCs from the outer membrane surface into the stripping gas. On the contrary, in a microporous membrane (e.g. polypropylene membrane) the VOCs directly diffuse through pores. The nonporous, hydrophobic silicone membrane is more selective toward organic compounds, and it reduces the diffusion of water through the membrane. When the stripping gas is to be introduced directly into a GC column or GC/MS the elimination of water is an important consideration.

Measurement devices based on membrane separation have been developed for different types of applications [44, 48, 49, 92-98]. VOCs from water samples have been directly introduced into mass spectrometers through a membrane without any GC separation [96-98]. An analysis system which combines membrane extraction followed by GC injection using a sampling valve has been reported [48, 49]. Although gas sampling valves can automatically make injections into a GC column, they have certain limitations in trace analysis. Only a small volume (few microliters to a milliliters) can be injected. A large injection causes excessive band broadening, while a small injection volume reduces sensitivity. As a result these systems have high detection limits and are not effective in monitoring at trace level.

5.1.2 On-line Microtrap

The sample introduction device is the most important component in GC instrumentation used for continuous, on-line monitoring. It should be able to make automatic, reproducible injections. Recently we have reported the development of an on-line microtrap (OLMT) for continuous monitoring of VOCs in air [30, 57]. The microtrap is a short length of small diameter tubing containing an adsorbent. The microtrap is directly connected in front of the analytical column. A flowing gas stream containing the VOCs is introduced directly into a GC column through the OLMT. As the stream passes through the OLMT, the VOCs are retained by the adsorbent in the microtrap. A pulse of electric current rapidly heats the microtrap to desorb the trapped VOCs. Due to its low thermal mass, the microtrap can be heated (and cooled) very rapidly. This rapid desorption generates a "concentration pulse" of VOCs that serves as an injection for GC separation. So, the OLMT is not only an automatic injection device but also a sample preconcentrator. Consequently, low detection limits can be achieved using an OLMT.

In this investigation membrane extraction was combined with the on-line preconcentration cum injection by a microtrap. A membrane module consisting of a single hollow fiber membrane was used to extract the VOCs from the water sample into an inert gas stream. The VOCs in the gas stream were concentrated using an OLMT and then injected into GC for analysis. Continuous monitoring of the VOCs in water was achieved with this on-line membrane extraction microtrap system (OLMEM).

5.2 Experimental

The schematic diagram of the experimental system is shown in Figure 43. Two different membrane module designs are possible using hollow fiber membrane:

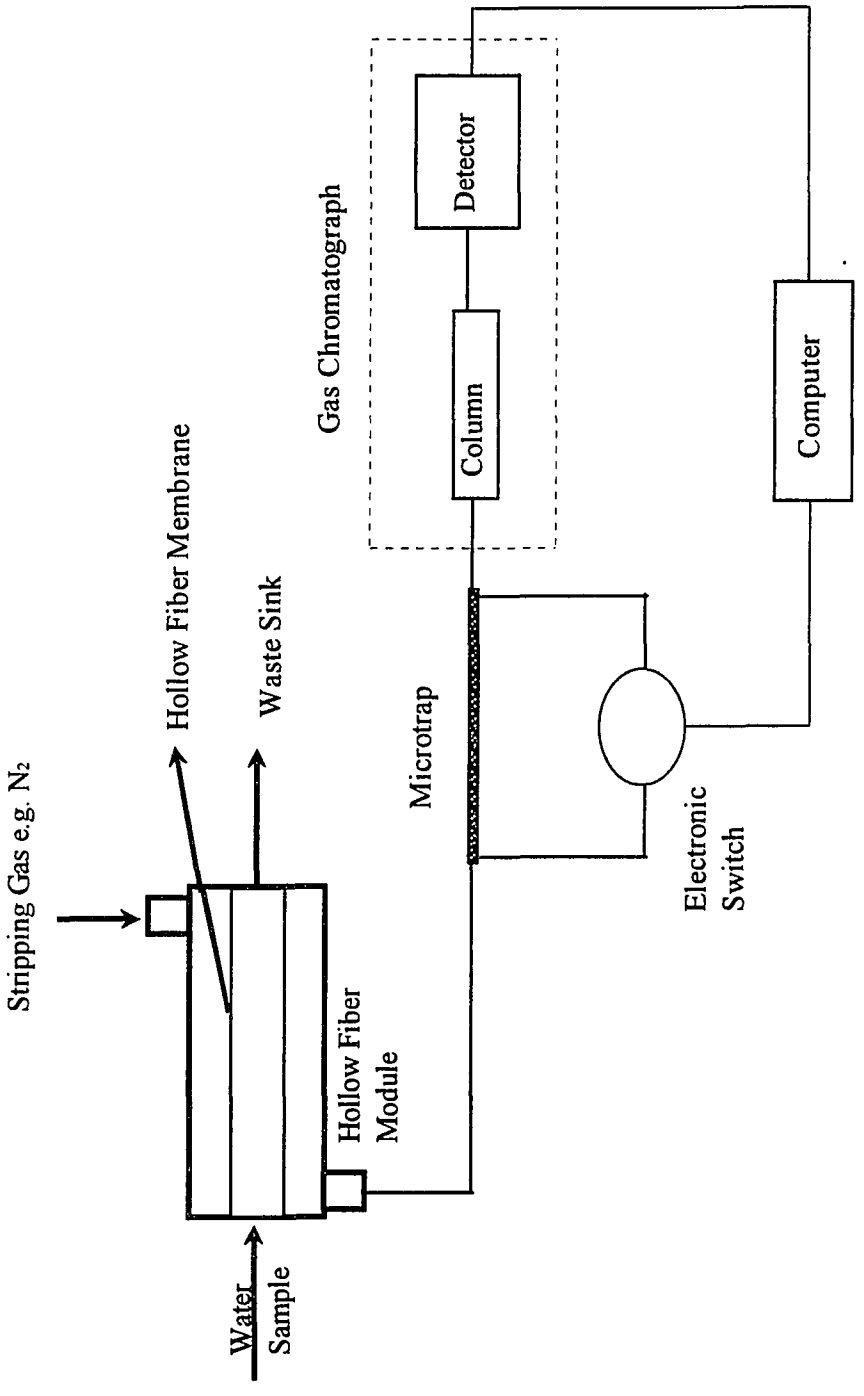


Figure 43 Schematic diagram of on-line membrane extraction microtrap system.

"flow-over" and "flow-through" [48, 96]. In flow-through configuration, the aqueous sample is passed through a hollow fiber membrane while the stripping gas flows on the outside. In flow-over configuration the water sample passes on the outside of the membrane. The membrane module here was operated in the "flow through" configuration. The membrane used in this study was Dow Corning Silastic medical grade tubing. The membrane size used was 0.012 in. i.d. x 0.025 in. o.d. (Dow Corning Corporation, Midland, Michigan). The membrane module consisted of a single hollow fiber. The membrane was connected to narrow bore stainless steel tubing of 0.015 inch outer diameter. To connect the hollow fiber membrane to the steel tubing, the end of the membrane was immersed in xylene for about 5 minutes. When it became swollen, 2 cm long membrane was carefully slipped over the tubing. After the solvent evaporated, the membrane shrank to form a tight fit. The connection point was sealed by silicone glue. The active length of the fiber was approximately 20 cm.

A Hewlett Packard 5890 Series II gas chromatograph (Hewlett Packard Company, Avondale, PA) equipped with a conventional flame ionization detector was used for analysis. A 30 m long DB-1 fused silica open tubular column from J&W Scientific Inc.(Folsom, CA) was used. The column inner diameter was 0.25 mm, and the stationary phase thickness was 1.0 μm. Typical flow rates were between 2 and 6 ml/min.

The microtrap was made by packing a 0.52 mm i.d. silica lined stainless steel tubing with 60 mesh Carbotrap C. This microtrap had a resistance of 0.1 Ω /cm and its length was 14 cm. The microtrap was connected to a variable power supply (20-50 V AC). A computer controlled electric switch was used to control the interval between pulses and also the time for which the microtrap current was turned on. Power resistors were put in series with the microtrap to limit the current

through it. More details of the microtrap and its operation are presented elsewhere [30].

5.2.1 System Operation

The aqueous sample was pumped through the membrane module using a HPLC pump (Altex, model 110A). Nitrogen (stripping gas) flowed countercurrent around the membrane fiber and carried the permeated VOCs to the microtrap. The microtrap was pulsed (or heated) at regular intervals, and corresponding to each pulse a chromatogram was obtained. Interval between pulses were anywhere from a few seconds to several minutes. In a typical operation the microtrap was heated with a 5-10 amp current for a duration of 500 to 1500 msec. All transfer lines were heated to 100°C to prevent any condensation of VOCs.

5.3 Results and Discussion

The operation of the analytical system is demonstrated in Figure 44 where a water stream containing 87 ppb each of benzene, toluene and ethyl benzene was continuously monitored. The water flowed continuously through the membrane module. Microtrap pulses were made at fixed intervals of time, and corresponding to each injection, a chromatogram of the three compounds was obtained. In this example, analysis was done every two minutes. Excellent reproducibility of peak height, peak shape as well as retention time was obtained. For twenty one consecutive injections, the relative standard deviations of peak area for benzene, toluene and ethyl benzene were 1.4%, 0.41% and 0.44% respectively. In fact the relative standard deviation was lower than that obtained by making direct injections using an conventional GC injection port (RSD was 2%). This shows that not only the microtrap injections, but also the membrane extraction process was

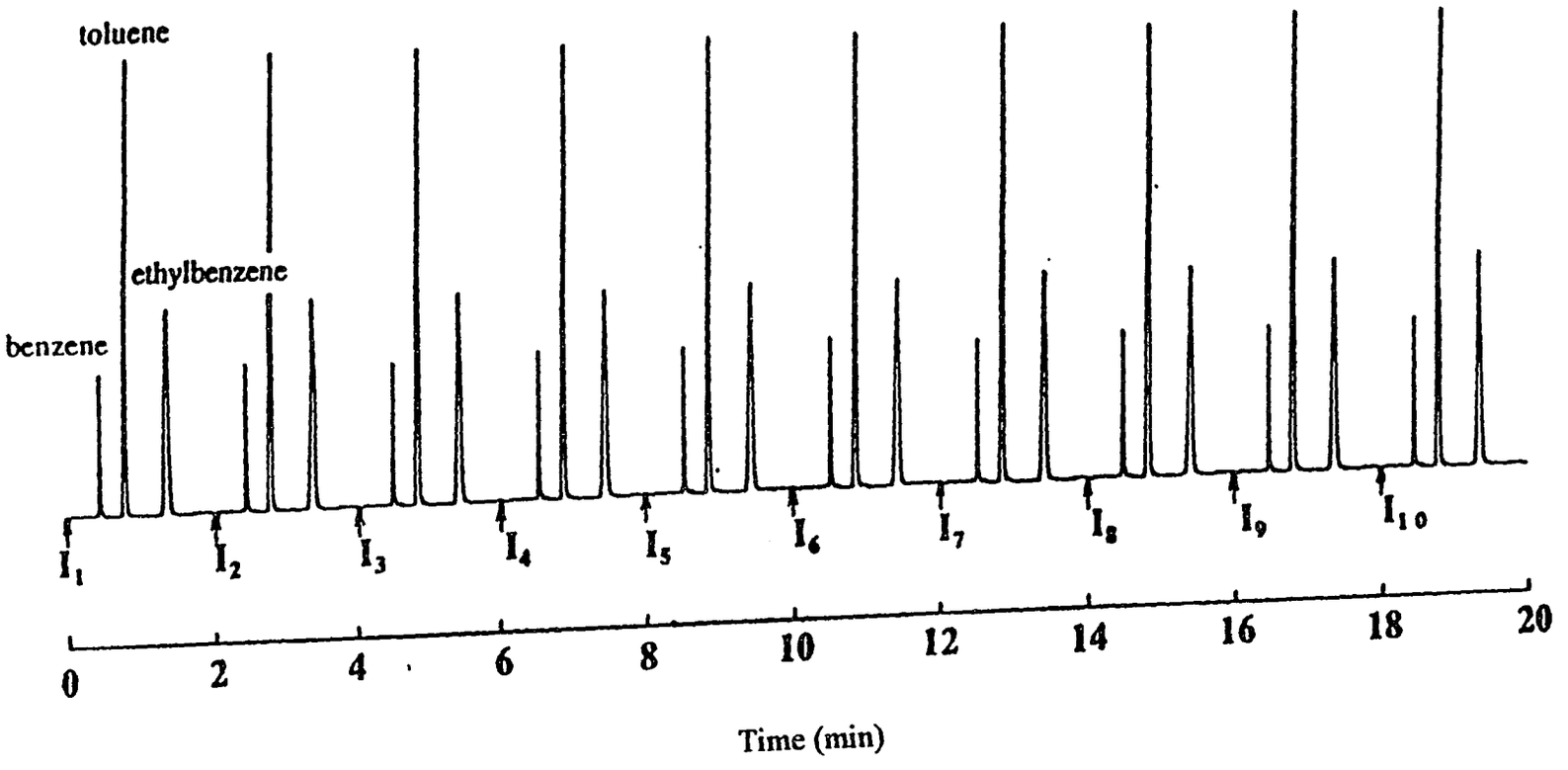


Figure 44 Continuous monitoring of a water stream containing 87 ppb each of benzene, toluene and ethylbenzene. Microtrap pulses were made every two minutes at points I_1, I_2, I_3 ... .

quite reproducible. The heating-cooling cycle of the microtrap is very short (less than 5 seconds) and it is capable of making injections every few seconds. How often injections can be made depends upon the time required for GC analysis. Hence, it is advantageous to reduce the separation time as much as possible.

As mentioned before, the microtrap acts as a sample concentrator. It accumulates VOCs during the interval between two pulses (referred to as a pulse interval). So, longer the interval, the larger amount of VOCs accumulated and the detector response to a microtrap pulse increases. Typical detector response as a function of pulse interval is presented in Figure 45. It is observed that as the time period increases, the response of the microtrap increases linearly until a maximum value is reached beyond which the response stays constant. The microtrap response can not be indefinitely increased because the microtrap contains a small amount of adsorbent, and retains the sample for only a short period of time before the sample breaks through. The analysis may be carried out quantitatively in the linear region or in the flat portion of Figure 45 [60].

5.3.1 Quantitative Aspects of The Analytical System

The calibration curves for several VOCs are presented in Figure 46. The linear relationship between system response and concentration was observed in the low ppb to high ppm range. Detection limits (at signal to noise ratio of 3) for some VOCs are presented in Table 6. It is seen that this system showed low detection limits. For example, the detection limit for trichloroethane using this system was 0.28 ppb as compared to 30 ppb when a cryogenically cooled gas sampling value was used in another study [49]. The non-polar, hydrophobic compounds showed a detection limit in the low ppb levels, whereas the detection limit for the water soluble compounds such as acetone and ethanol was considerably higher.

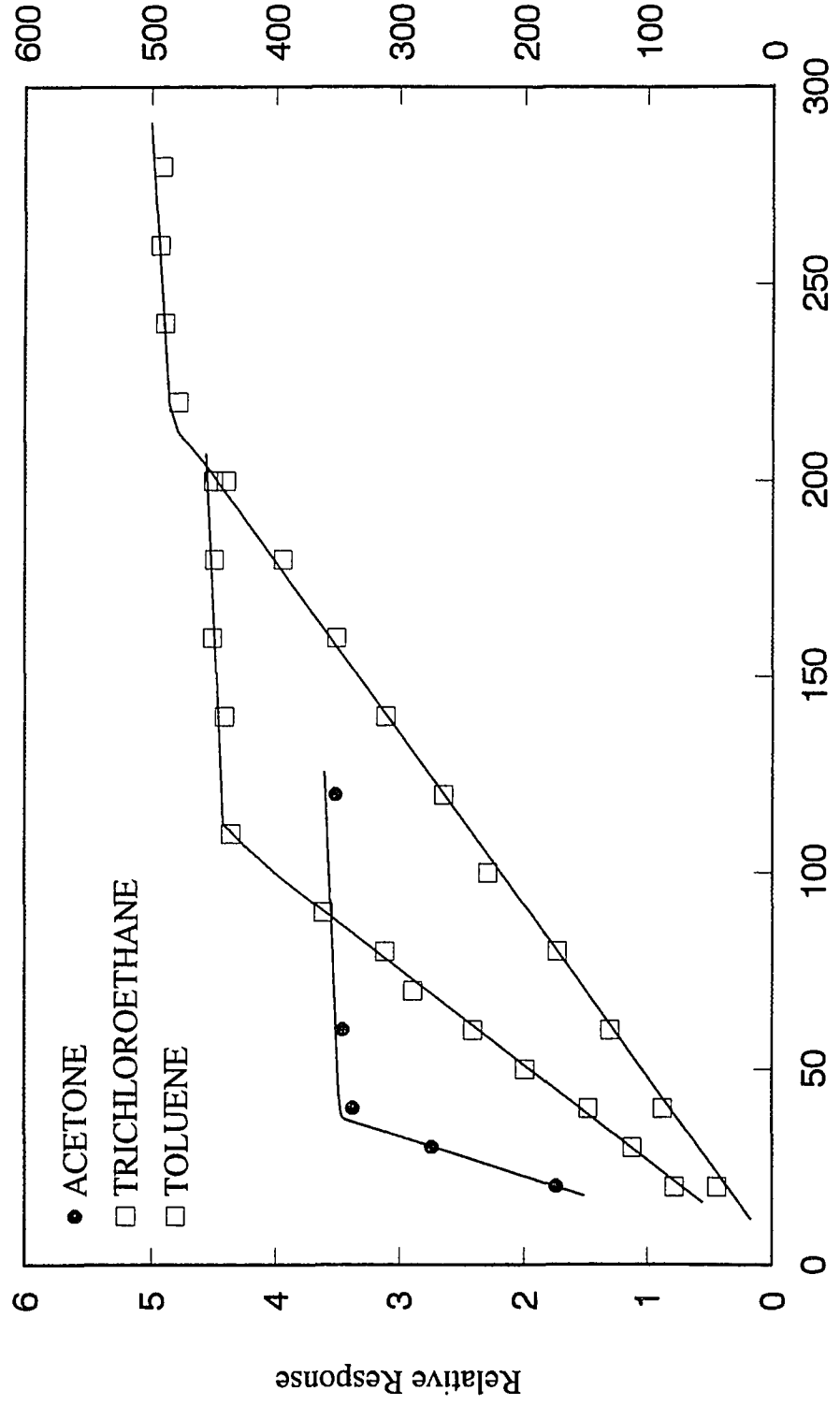


Figure 45 Response of the analytical system as a function of interval between microtrap pulses. The flow rate of water was 1 ml/min, the flow rate of stripping gas was 2 ml/min and the temperature of membrane module was 80°C.

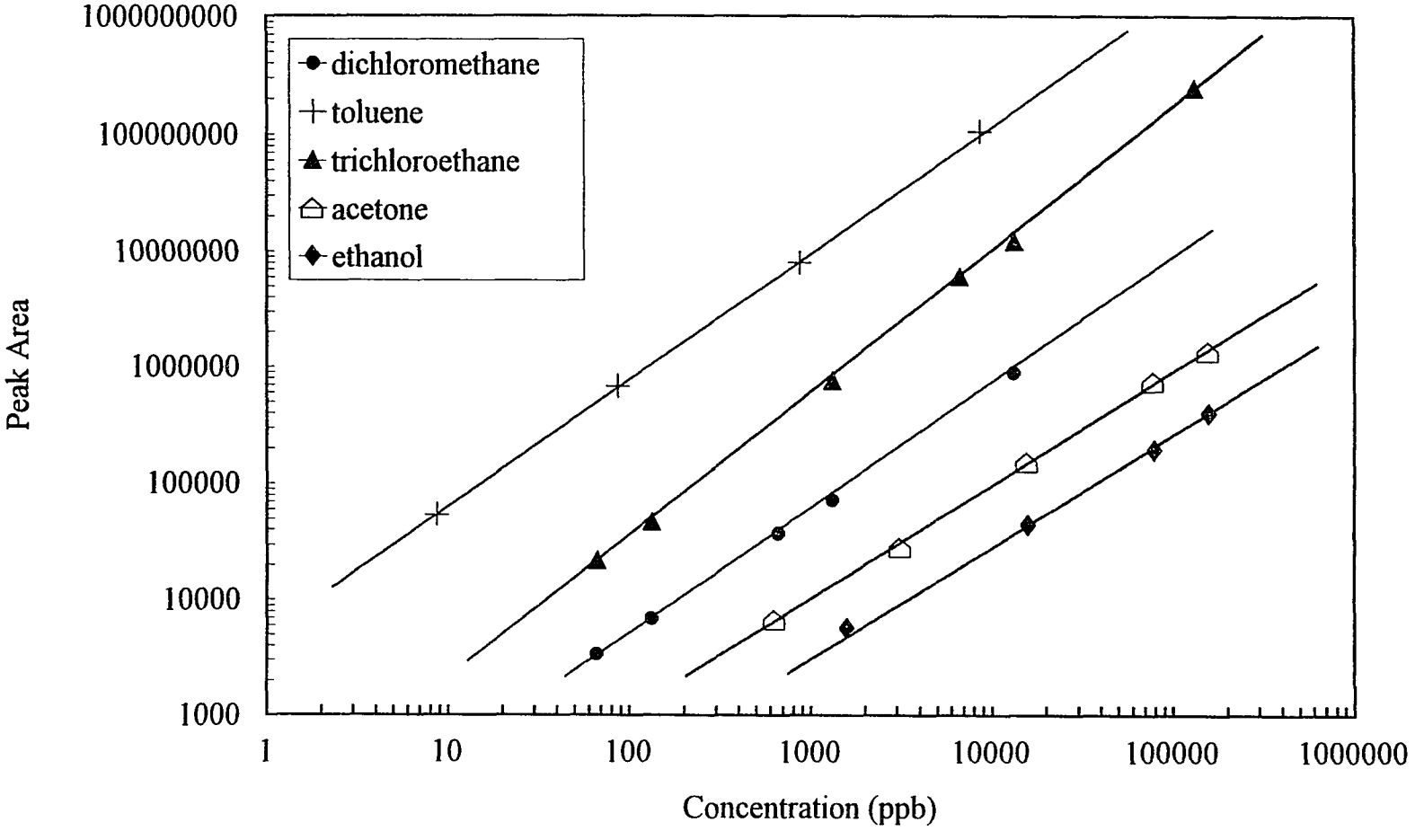


Figure 46 Calibration curve for typical VOCs. The flow rate of water sample was 1 ml/min, the pulse interval was 2 minutes, the flow rate of stripping gas was 2 ml/min, the temperature of membrane module was 80°C and the column temperature was 70°C.

The detection limit depends upon the extraction efficiency of the membrane as well as the preconcentration effect of the microtrap. By increasing the pulse interval, more analyte can be accumulated in the microtrap and consequently the detection limit can be lowered. The detection limits presented in Table 7 correspond to a pulse interval of 2 min. The detection limit could also be reduced by subambient cooling of the microtrap [30]. However, for a continuous monitoring device, subambient cooling is expensive and cumbersome, and was avoided in this application. It may be possible to further lower the detection limits by redesigning the membrane module with a longer hollow fiber or by using multiple hollow fibers so that higher extraction efficiency can be obtained.

The membrane extraction efficiency may be expressed as enrichment factor [44], E:

$$E = \frac{\text{mole fraction of analyte in stripping gas}}{\text{mole fraction of analyte in aqueous solution}} \qquad (5.1)$$

The enrichment factor was experimentally determined by measuring the concentration of the VOCs at the inlet and the outlet of the membrane module and results are presented in Table 7. The enrichment factor was seen to vary between 4.1 and 65.1. As expected, the compounds with low enrichment factors have high detection limits, e.g., acetone and ethanol.

The membrane extraction process is analogous to liquid-liquid extraction and the partition coefficient of the VOCs between the membrane and aqueous phase determines the enrichment factor. Experimental values of the partition coefficient between the membrane and the aqueous phase are not available. So, the partition coefficients for these VOCs in the hexane/water and octanol/water systems [99] are listed in Table 7. Partition coefficient into the silicone membrane has been reported to be somewhat similar to the hexane/water system [92]. A correlation between enrichment factor and partition coefficient, and an inverse

relation between partition coefficient and detection limits were seen. For example, acetone and ethanol have low partition coefficients, low enrichment factors, and high detection limits.

Table 7 Detection Limits and Enrichment Factors for Different VOCs

Compounds	Detection Limits (ppb) [a]	Enrichment Factor [b]	Partition Coefficient log $P_{octanol}$ [99]	Partition Coefficient log P_{hexane} [99]
Toluene	0.042	65.1	2.11	2.85
Trichloroethane	0.28	61.8	2.31	not available
Hexane	1.45	44.1	1.88	not available
Dichloromethane	7.75	42.4	1.68	not available
Acetone	61.1	7.5	-0.24	-0.92
Ethanol	212	4.1	-0.32	-2.26

[a] pulse interval is 2 minutes.
[b] water samples were analyzed by direct GC injection. The temperature of membrane module was 80°C and water flow rate was 1 ml/min.

5.3.2 Optimization of Membrane Extraction Conditions

To achieve high sensitivity, it is desirable to transport as much of the VOCs as possible through the membrane into the GC. Two mechanisms control the transport of VOCs: (1) diffusion through the membrane; (2) mass transfer in the aqueous phase. The diffusion of VOCs through a membrane is governed by Fick's law of diffusion [100]. At steady state, the rate of diffusion per unit surface area per unit time is given as F:

$$F = - D \partial C/\partial X \quad (5.2)$$

where D is the diffusion coefficient of the VOCs in the polymeric membrane, and $\partial C/\partial X$ is the concentration gradient across the membrane. For a hollow fiber membrane:

$$\partial C/\partial X = (C - K_1 C_o)/L \quad (5.3)$$

Where K_1 is the partition coefficient between the membrane and the aqueous phase , C_o is the concentration of VOCs in aqueous phase, C is the concentration of VOCs on outside surface of membrane and L is the membrane thickness.

When the flow rate of the stripping gas is high enough, C is close to zero. K_1C_o represents the concentration of the analyte on the inside membrane surface which is in contact with the aqueous sample. Under these conditions:

$$F = DK_1C_o/L \quad (5.4)$$

According to this equation, F depends upon D and K_1 which in turn depend upon temperature. Thus, the temperature of the membrane module is an important factor which will effect the system response.

The flow rate of aqueous phase in the membrane is another important factor because the mass transfer in the aqueous phase depends largely upon it. The inorganic salt concentration (or ionic strength) and pH of the water sample are other parameters which can effect the system response.

Effect of Flow Rate: The effects of sample flow rate on the detector responses for dichloromethane and hexane at two different temperatures are shown in Figure 47. As flow rate is increased, the system response increases because at higher flow rate there is more mixing at the water/membrane interface, and the formation of a boundary layer is reduced or eliminated. At higher flow rates, the rate limiting step is the mass transfer through the membrane rather than migration of the analyte

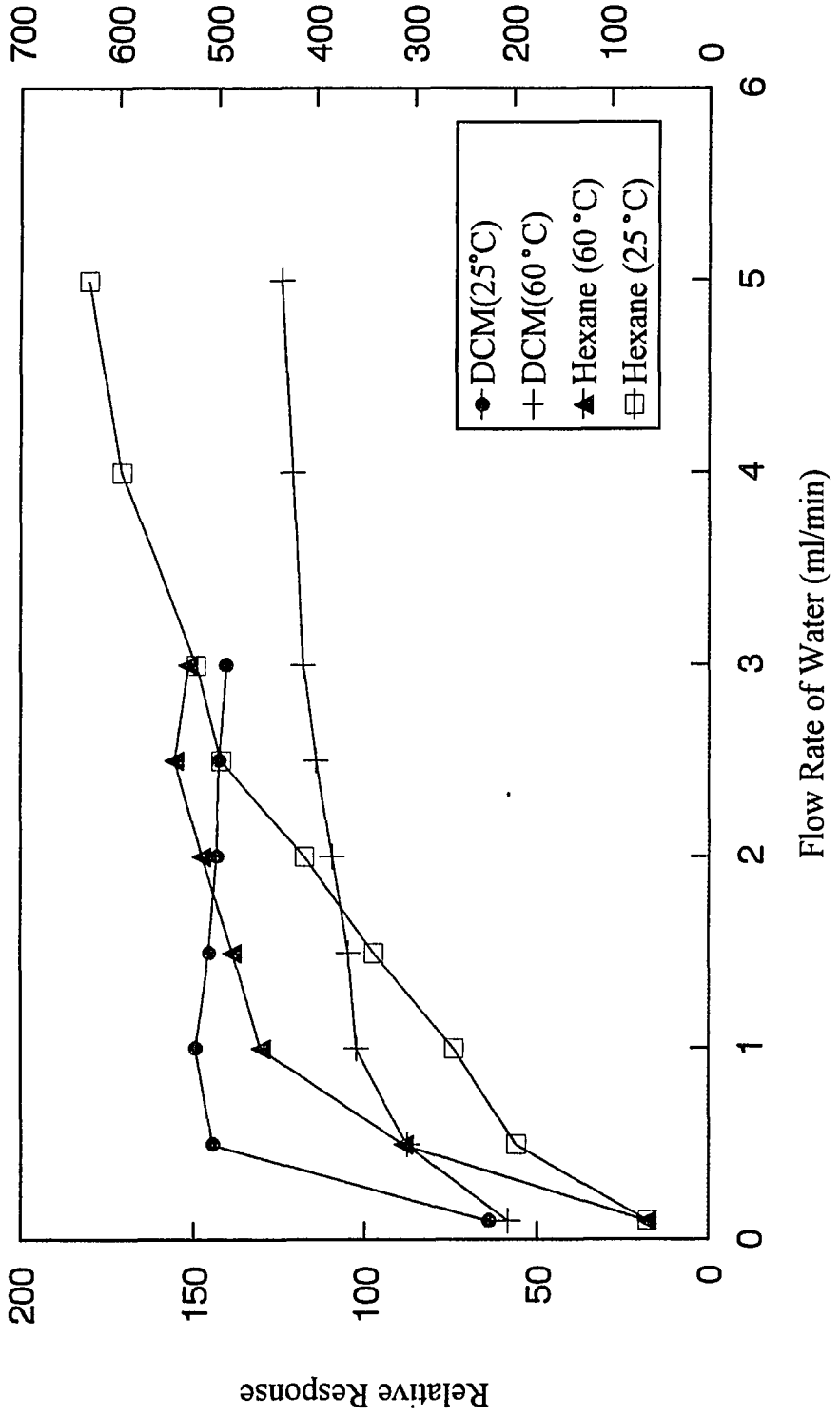


Figure 47 Response of analytical system as a function of flow rate of water. Pulse interval was 2 minutes, the flow rate of stripping gas was 2 ml/min and the temperature of membrane module was 80°C.

through aqueous phase. Thus, increasing the flow rate beyond a certain value has a negligible effect on system response.

For the components that permeate rapidly through the membrane, mass transfer in the aqueous phase is the rate limiting step. Mass transfer is better in a turbulent flow rather than laminar flow. Laminar flow turns turbulent at Reynolds number between 2000-3000 [101]. Reynolds number is calculated by the equation:

$$N_{Re} = vd\rho/\mu \qquad (5.5)$$

here, d is the inner diameter of the membrane, v is the linear velocity of water stream, ρ is the density of the water stream, μ is the viscosity of water stream. The membrane used here has an inner diameter of 0.012 inch and the N_{Re} reaches 2500 at a flow rate of 38 ml/min. At such a high flow rate, there is significant pressure drop across the narrow diameter hollow fiber. The silicone fibers are relatively delicate and are unable to withstand such pressure drops and can easily tear, especially at the connections. Another problem at high flow rate is that the residence time is short and only a small fraction of the analyte is extracted from the sample stream. To increase turbulence without increasing flow rate, the membrane tubing can be packed with glass beads [102]. However this method may increase the memory effect of the membrane module and will be addressed in future studies.

Effect of Temperature: The effect of the water temperature on the analytical system response is shown Figure 48. It was seen that the responses initially increased with the increase in temperature. Above a temperature of 60°C for dichloromethane and 80°C for trichloroethane and chloroform, the responses decreased with increase in temperature. So, when response was plotted as a function of temperature the curve passed through a maximum point. The maximum

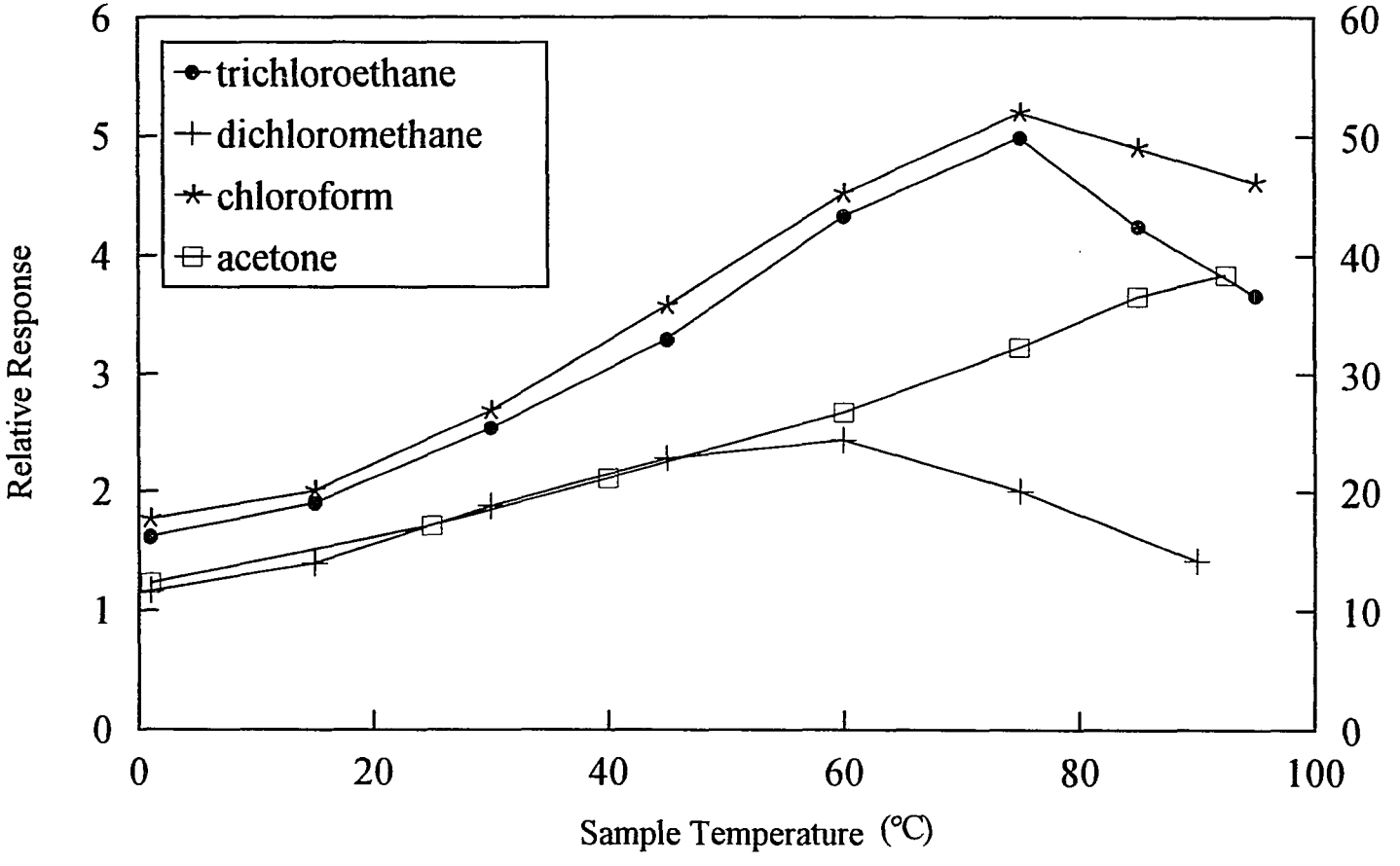


Figure 48 Response of analytical system as a function of water temperature. The flow rate of sample was 1 ml/min. Pulse interval was 2 minutes. The flow rate of stripping gas was 2ml/min. The column temperature was 70°C.

point for all the compounds with the exception of acetone was in the temperature range studied here. The reason for such behavior is that permeability is a function of rate of diffusion (F) as well as the solubility of the analyte in the membrane [100, 103]. The diffusion coefficient D increases with temperature and an Arrhenius type relationship exists:

$$D = D_o \exp.(- E_d/RT) \quad (5.6)$$

where D_o is the diffusion coefficient at reference temperature, T is temperature and E_d is the activation energy for diffusion. However, solubility of the organic analyte in the membrane decreases with increase in temperature:

$$S = S_o \exp.(-\Delta H/RT) \quad (5.7)$$

where ΔH is the apparent heat of solution, which has a negative value for organic liquid.

The initial increase of system response with increasing temperature is due to the increased rate of diffusion. However, as temperature is further increased the decrease in solubility becomes the dominant factor and the system response begins to decrease.

Effects of Salinity: Environmental samples may contain inorganic ions such as K^+, Na^+, Cl^- etc. For example, in typical surface water and ground water, the total ionic strength may be of the order of 0.01 mol/l and 0.05 mol/l respectively, whereas in sea water the ionic concentration may be as high as 0.5 mol/l. The effect of ionic strength on the system response was studied in the concentration range of 0.0 to 4.0 mol/l using NaCl. The effect of salinity on ethanol, acetone, toluene and dichloromethane are shown in Figure 49. In the low concentration range (0-0.4 mol/l), the response was unaffected by salt concentration. However, at higher concentrations (NaCl > 0.4 mol/l), the responses of toluene and

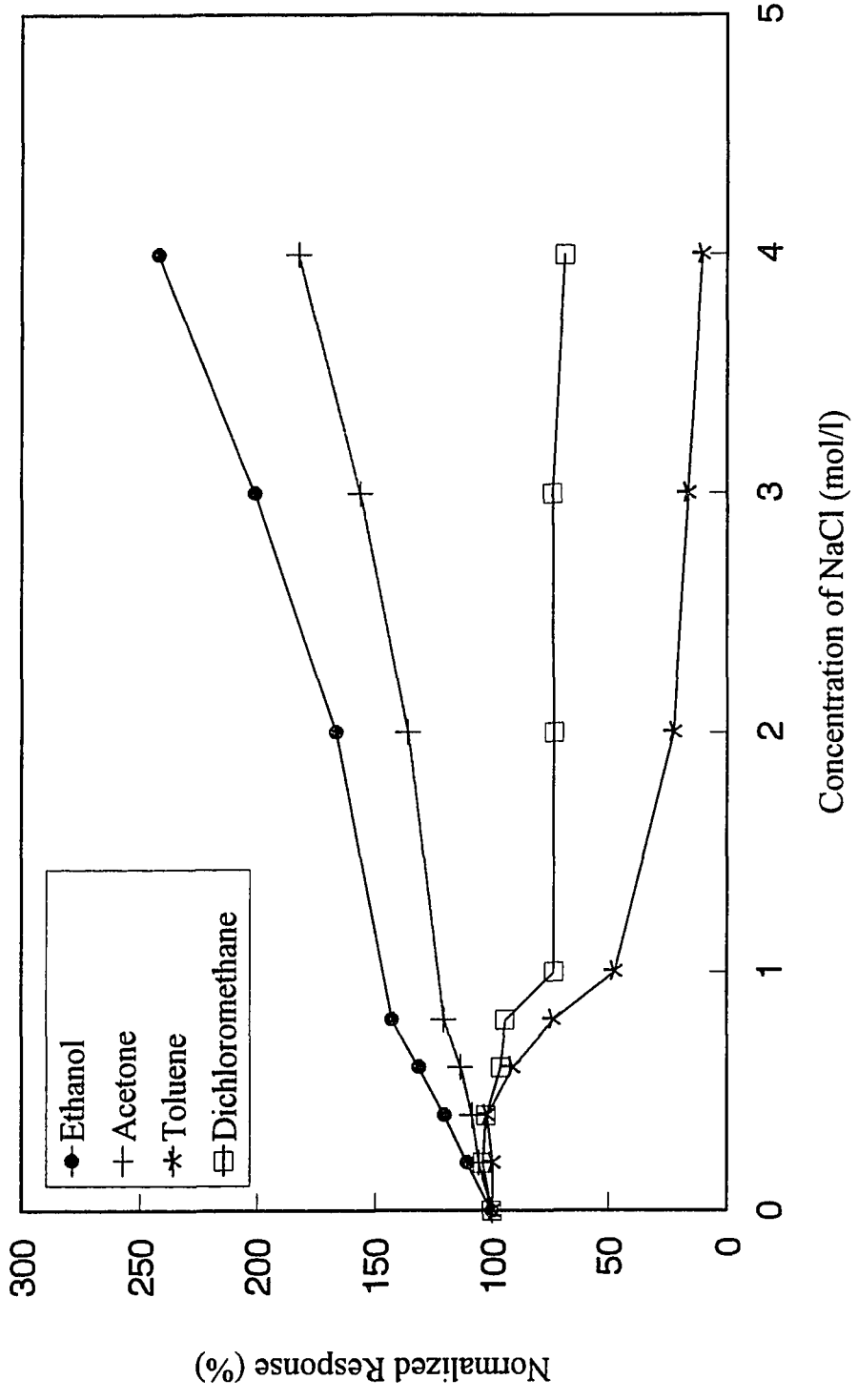


Figure 49 Effect of ionic strength on system response for different VOCs. The sample response of zero ionic strength is considered 100%. The concentration of toluene and dichloromethane were 1 ppm and the concentration of acetone and ethanol were 5 ppm.

dichloromethane decreased with the increase of sodium chloride concentration, but the responses of acetone and ethanol increased with the increase of sodium chloride concentration. It seems that high ionic strength solutions, each component behaves differently. From a practical point of view, one seldom encounters ionic strength greater than 0.1 mol/l where the system response is not a function of ionic strength. At higher ionic strength recalibration of the system would be necessary.

Effect of pH: Usually the pH of environmental samples are in the range of 2.5 to 10.5. The response of two test compounds, toluene and ethanol, were studied in the pH range of 1.5 and 12.5. Both these compounds did not show any significant variation in response with pH (Figure 50). This is expected for most VOCs although pH may turn out to be an important factor for organic compounds which are acidic or basic [92].

5.4 Summary

The on-line membrane extraction microtrap system can be used to provide continuous, on-line monitoring of (VOCs) in water samples at ppb level. The microtrap is effective as an automatic, on-line, sample preconcentrator cum injector. The detection limits for most of the tested VOCs were at the low ppb level. The detection limits for the water soluble, polar compounds was relatively higher than the nonpolar ones.

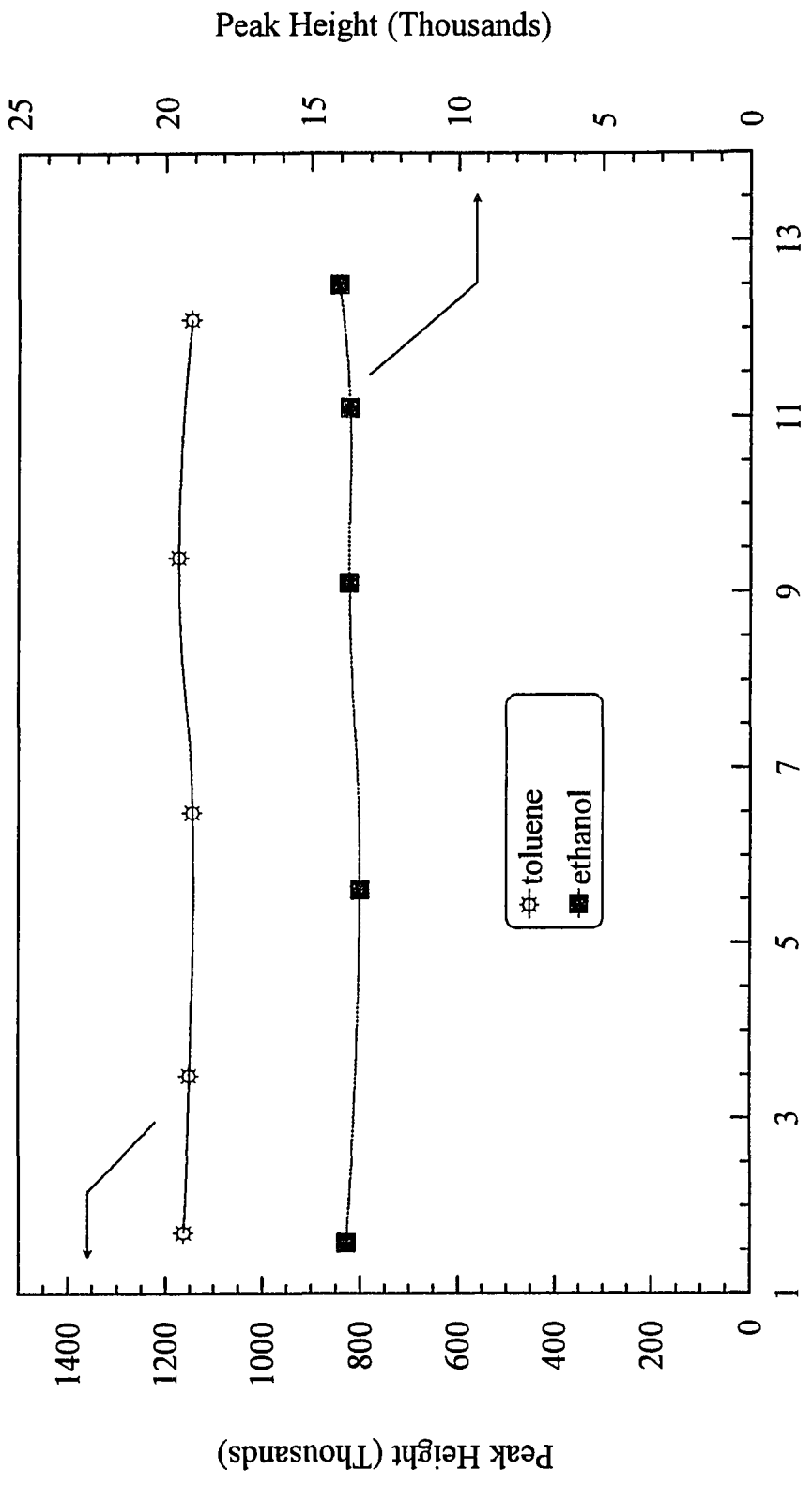


Figure 50 Effect of pH value of water sample on response. The concentration of toluene was 1 ppm and the concentration of ethanol was 5 ppm. The flow rate of water sample was 1 ml/min.

CHAPTER 6

ON-LINE MONITORING OF NONMETHANE ORGANIC CARBON IN GAS STREAM USING MICROTRAP BASED INJECTION SYSTEMS

6.1 Background

The list of volatile organic compounds (VOCs) includes a variety of alkyl substituted aromatic hydrocarbons, as well as organic molecules containing different functional groups. The VOCs in the environment may be hazardous to public health even at very low concentration since many of the VOCs, such as aromatic and halogenated compounds are toxic, mutagenic, and/or carcinogenic. The VOCs may present in soil, sludge, water and air. However, the VOCs eventually enter into air and become air pollutants since they can evaporate readily. Therefore the measurement of VOCs in air has been becoming a very important issue.

Nonmethane organic carbons (NMOC) are total organic compounds, except methane. NMOCs are major pollutants in atmosphere. Hydrocarbons are one of the major ingredients in the photochemical reaction which generates smog on the urban and regional scale. Organic acids, one type of NMOC, and products of NMOC oxidation contribute to acidic rain. NMOC also contributes to global warming and destruction of ozone layer. NMOC can also come from incineration processes as products of incomplete combustion (PIC) and incomplete oxidation. Therefore the measurement of NMOC in atmosphere and incineration stack gas is very important to control pollution sources and to understand atmospheric chemistry [104-111].

EPA standard method 25 was developed in the mid 1970's as a means of quantifying NMOC emission from stationary sources such as incineration facilities and the painting industry [112]. After gas samples are collected and sent to lab, a nonmethane organic carbon analyzer, which is an oxidation/reduction gas chromatograph, is used to perform a quantitative measurement. In the usual

nonmethane organic carbon analyzer, one milliliter of gas sample is introduced into a separation column by a multiport sampling valve. The column is packed with a stationary phase which separates VOCs from permanent gases such as CO_2, CH_4 and CO. After CO_2 peak elutes, a backflushing thermal desorption is applied to the separation column to transfer the VOCs into a oxidation reactor. Thus, each carbon in hydrocarbon is first oxidized to CO_2 in the oxidation unit and then is converted into CH_4 in a reduction unit. Finally a FID gives the response of methane. This method does not speciate VOCs, and also gives a response for carbon-containing permanent gases. However, air samples from incineration stack contain a high concentration of carbon dioxide which has response in FID after passing through reduction reactor. Actually, the column shows poor separation of NMOCs from high concentrations of carbon dioxide, especially over 8%. Another major problem is that the detection limits are not low enough, since the injection volume is limited to keep good separation.

Continuous on-line monitoring of manufacturing processes is becoming more and more important for industry to comply with today's and future environmental laws [7, 11]. Two factors which are largely responsible for the drive towards real-time analysis are regulatory compliance and product quality. The conventional analytical method, which involves grabbing a sample, transporting it to the lab, and sample preparation, is not suitable for continuous monitoring since whole process takes hours or days for waiting and analysis. Continuous, on-line analysis can eliminate or minimize the error due to sample handling since there is one step for sampling, sample preparation and injection. There is no delay between sampling and analysis. Therefore, the major component for an on-line analyzer is the sampling and injection device. In air analysis, a conventional multiport valve is most popular injection device. Cone and coworkers [113] developed a total hydrocarbon continuous emission monitor for incineration stack gas. However, the

valve can inject only a small part of sample into analytical system. It can not perform a trace level analysis.

On-line injection devices based on microtrap technology have been developed and used in continuous monitoring of volatile organic compounds in air using GC [30, 31]. A microtrap is a short tubing packed with one adsorbent. When a gas sample continuously passes through on-line microtrap (OLMT), the microtrap can selectively retain the volatile organics since the permanent gases such as CH_4, CO_2 and H_2O pass through and vent out. The trapped organics are injected into GC column by thermal desorption. Because the thermal mass of microtrap is very small, this thermal desorption is very rapid and serves as a GC injection. The microtrap can only retain the organics for a period of time which depends on the breakthrough volume. Basically, the microtrap is an on-line injection device as well as a preconcentrator. Several configurations of the injection based microtrap system have been reported. The on-line microtrap (OLMT) has the highest sensitivity. But it does not isolate the GC analytical system from the sample stream. In the sequential valve microtrap system (SVM), a large volume of sample or multiple small injections were injected into microtrap and the microtrap retained and concentrated the volatile organics. This configuration can be applied to various analytical systems.

In this approach, a multi-bed microtrap has been developed to concentrate the NMOC and also serve as the column to separate the organics from permanent gases. When a sample containing NMOC continuously passes through the microtrap injection device, the NMOC are trapped selectively and the permanent gases are vented. Then a thermal pulse is applied to release the NMOC to the system. Thus, a continuous, on-line monitoring system for NMOC in air has been developed. The parameters which affect the microtrap performance have been investigated. The exhausted gas from a catalytic incineration was continuously monitored by this microtrap based NMOC analyzer.

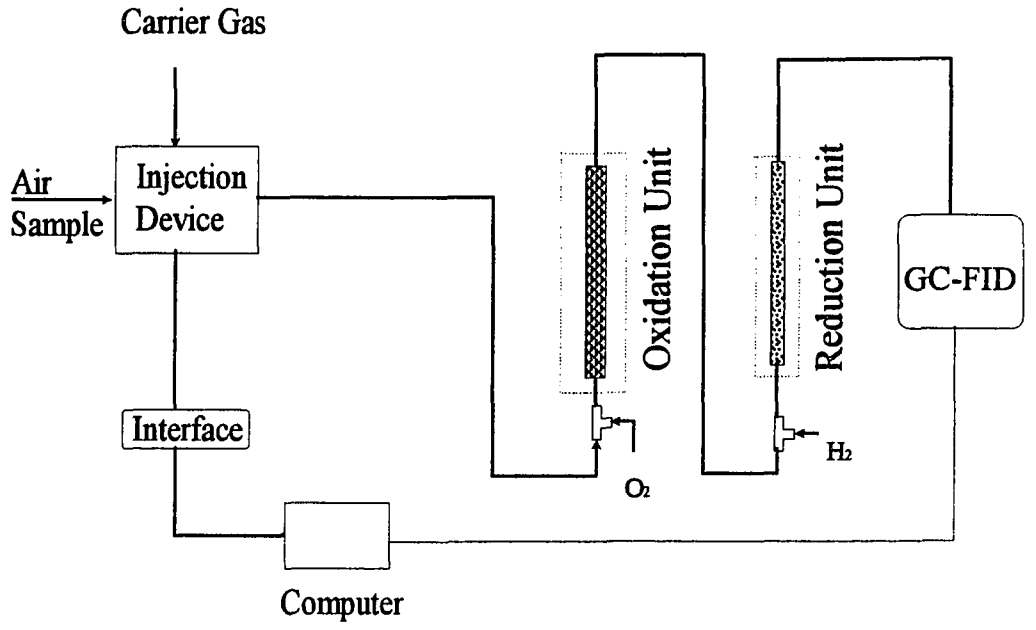
6.2 Experimental

6.2.1 Reagent and Materials

The organic solvents were reagent grade from Aldrich Chemical Company (Milwaukee, WI). Absorbents such as Carbotrap™ C and Carbosieve™ S-III came from Supelco Company (Bellefonte, PA). The homemade standard gases were prepared in 6-L evacuated canisters by injecting pure liquid organic solvent and filling with dry zero nitrogen from Spectra Gases Inc. (Newark, NJ) to 40 psi pressure. The gases were verified by comparison with a standard gas from AIRLIQUIDE Inc. (Morrisville, PA). The simulated incineration stack gas from AIRLIQUIDE (Morrisville, PA) contains 1 ppm of benzene, trichloroethane, toluene, ethylbenzene; 9.27% of CO_2, 10.9% of O_2, 164 ppm sulfur dioxide, 75 ppm of CO and balance nitrogen. Propane standard gas from AIRLIQUIDE (Morrisville, PA) contains 1.1 ppm of propane in nitrogen.

6.2.2 Instrumentation for Microtrap Based NMOC Analyzer

A schematic diagram of the continuous monitoring system used in this study is presented in Figure 51. The gas sampling valve was a six-port air actuated valve with a digital interface (Valco Instruments Co. Inc., College Station, Texas). Two kinds of microtrap were used: one was made from silica lined stainless steel tubing (Restek Co., Bellefonte, PA) and packed with Carbotrap™ C. The inner diameter of this microtrap is 0.54 mm and the length is 9 inch. The other one is 0.90 mm inner diameter and six inch long stainless steel tubing. This tubing was used to make a multi-bed microtrap which was packed with Carbotrap™ C, Carbotrap™ B and Carboseive™ S-III. The microtrap was connected to a variable power supply. A computer controlled electric switch was used to control the interval between pulses and the pulse time. Power resistors were put in series with the microtrap to



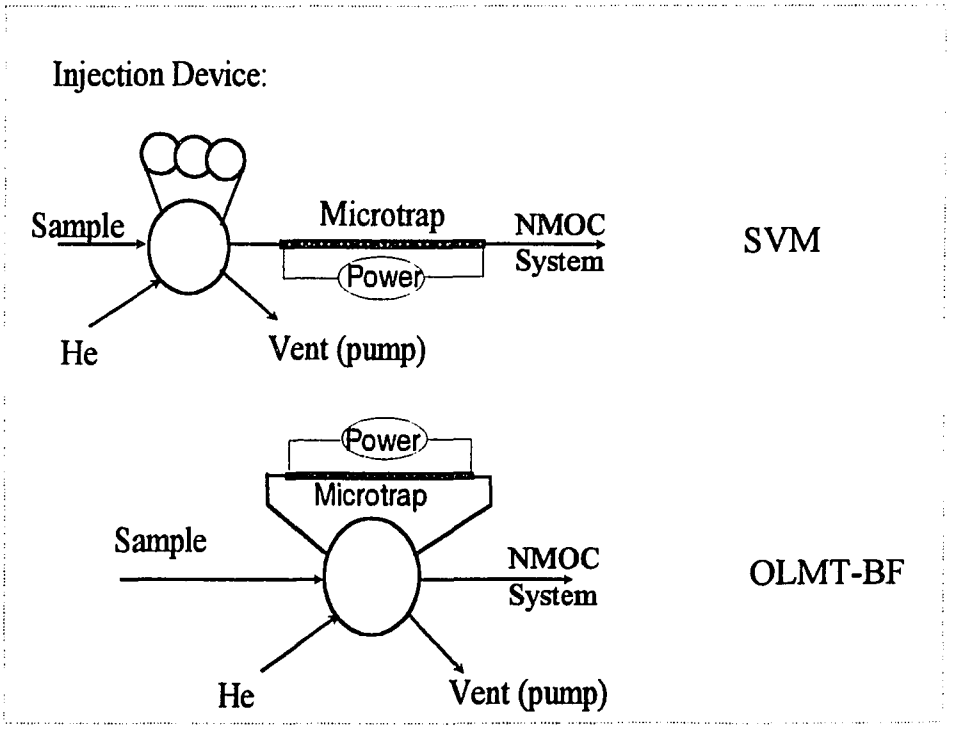


Figure 51 On-line microtrap based NMOC Analyzer.

limit the current through it. More detail of the microtrap and its operation are presented elsewhere [30, 31].

The oxidation reactor was a 1/4 inch stainless steel tube about 4 inch long packed with Chrome Alumina. This reactor was put in a furnace (LINDBERG, Watertown, WI). The reduction unit was a 1/4 inch OD quartz tube installed in the GC injection port. The reducing catalyst was 10% Nickel Nitrate on Chromosorb G AW 100/120 (Varian, CA). The temperature of reduction unit can be controlled from the GC panel. The typical operation temperatures for the oxidation unit and reduction unit were 650 °C and 380 °C respectively.

A Hewlett Packard 5890 Series II gas chromatograph (Hewlett Packard, Avondale, PA) equipped with a conventional flame ionization detector (FID) was used for this study.

6.3 Results and Discussion

Figure 52 and 53 present a typical chromatogram for on-line monitoring of NMOC in simulated stack gas by microtrap NMOC system. The sample stream contains 1 ppm of benzene, trichloroethane, toluene, ethylbenzene, 9.27% of CO_2 and other permanent gases. This gas stream continuously flowed through the microtrap based injection device. The microtrap selectively retained organic compounds. But CO_2, CO, H_2O, O_2, N_2 and other permanent gases break through immediately and vent out. In the sequential valve microtrap mode, 8 milliliter of sample was injected into the microtrap by a six-port valve and the hydrocarbons in gas sample were trapped by microtrap. But a large amount of carbon dioxide was flooding in the microtrap. Although CO_2 has very low breakthrough volume, it takes one or two minutes to strip the CO_2 out of the microtrap. After about 2 minutes delay time, the microtrap was heated to release hydrocarbon into NMOC system. Therefore, in Figure 52 a large permanent gas peak came out first and then a NMOC peak appeared. In this system, the microtrap can only trap the hydrocarbon

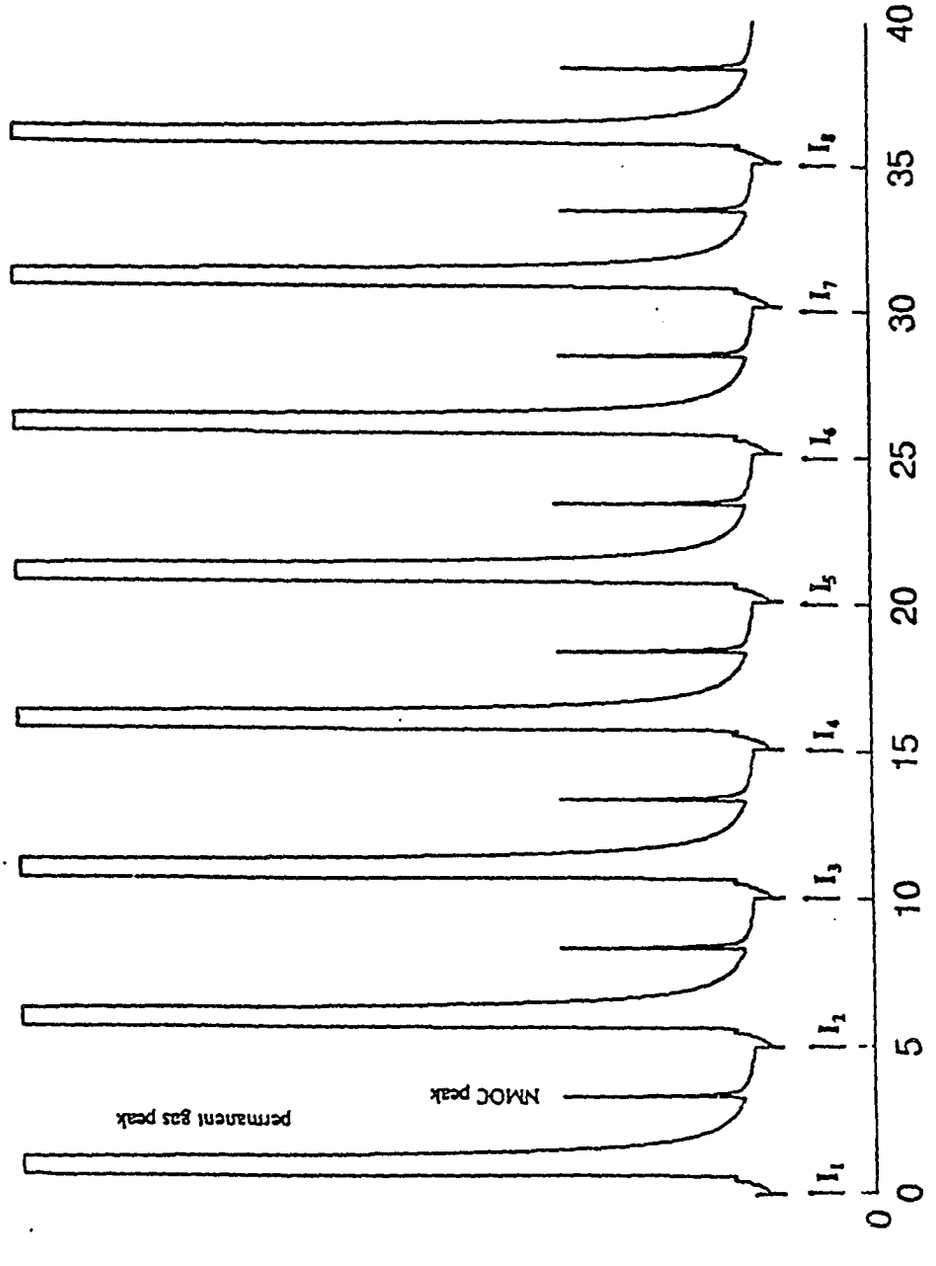


Figure 52 Continuous monitoring of simulated stack gas using sequential valve microtrap NMOC analyzer. The volume of sample loop was 8 ml and a 9 inch long 0.53 mm i.d. microtrap packed with Carbotrap C was used. The pulse interval was 5 minutes.

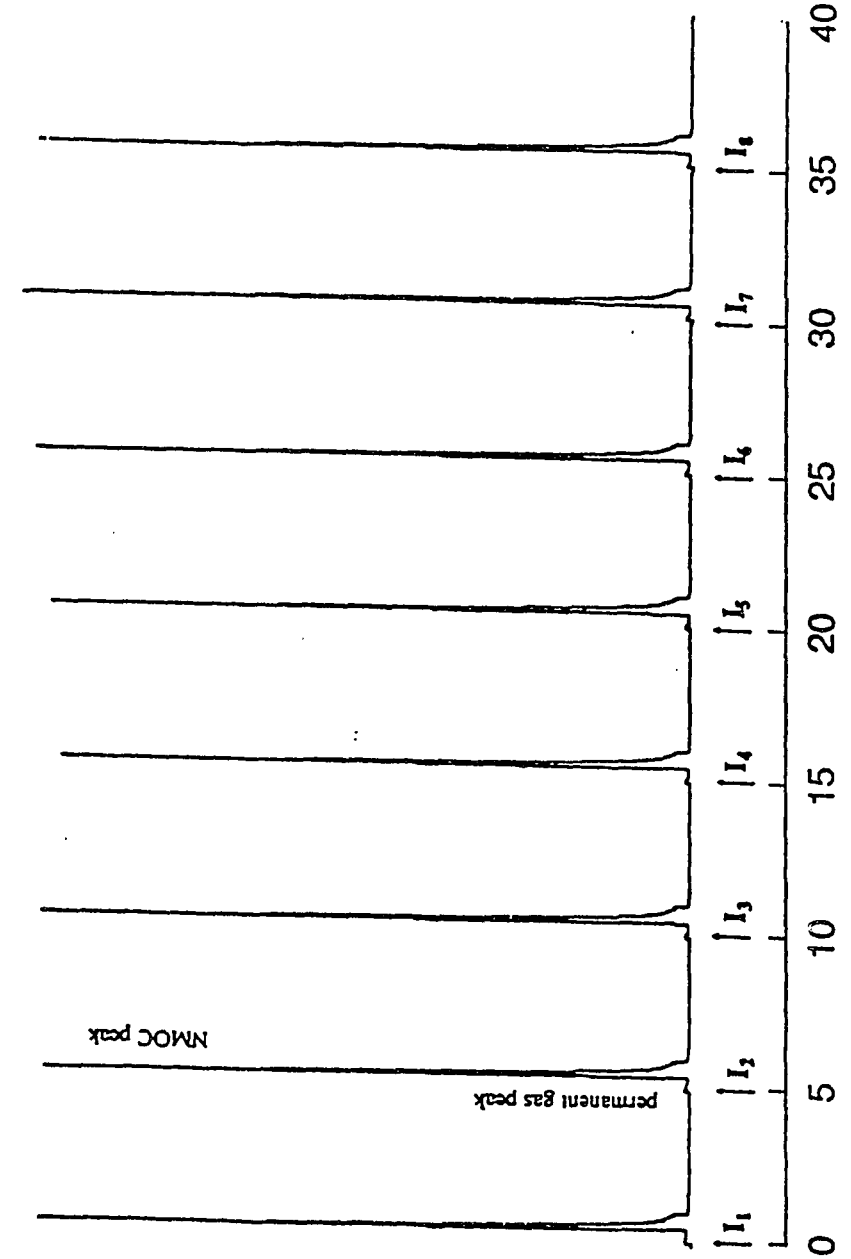


Figure 53 Continuous monitoring of simulated stack gas using OLMT-BF NMOC analyzer. A 9 inch long 1.5 mm i.d. multibed microtrap packed with Carbotrap C, Carbotrap (B) and Carbosieve S-III in series was used. The flow rate of sample was 6 ml/min and the pulse interval was 5 minutes.

for a short time since it was only packed with one adsorbent, Carbotrap™ C, which has small surface area. However, this microtrap has enough holding capacity for measuring common painting industry solvents such as hexane, toluene and cellosolve acetate. On other hand, the microtrap has small thermal mass. It only takes 100 ms to 1000 ms to desorb the NMOC from the microtrap by a pulse heating. So the NMOC peak was very sharp.

In the on-line microtrap-backflushing system (OLMT-BF), a multi-bed microtrap replaces a sample loop in a valve. In loading status, the sample stream continuously flowed through a multi-bed microtrap. The NMOC was retained by the microtrap and carbon dioxide, carbon monoxide and other gases were vented out. When the valve is in injection mode, a pulse heating released the NMOC into detection system. The multi-bed microtrap can retain organic compounds of varying volatiles, from C_3 to C_{16} since it was packed with three kinds of adsorbents: Carbosieve™ S-III for very light hydrocarbons, Carbotrap™ C for middle sized compounds and Carbotrap™ C for heavy compounds. The thermal desorption was completed using backflushing technique and will be discussed later.

6.3.1 Calibration and Detection Limit

The NMOC analyzer is designed to have an equivalent response for each carbon in various organic compounds since each carbon in a sample is converted to one CO_2 and then one CH_4. In Figure 54, four point standard gases were made from different types of compounds. First point was 0.1 ppm of hexane. Second point was 1 ppm of benzene. Third point was 3 ppm of 2-butoxy ethanol and forth was 15 ppm of trichloroethane. Straight lines were obtained for both SVM and OLMT-BF systems. However, the sensitivity of OLMT-BF system is much higher than SVM system in the same injection intervals since the OLMT-BF system has a larger injection volume.

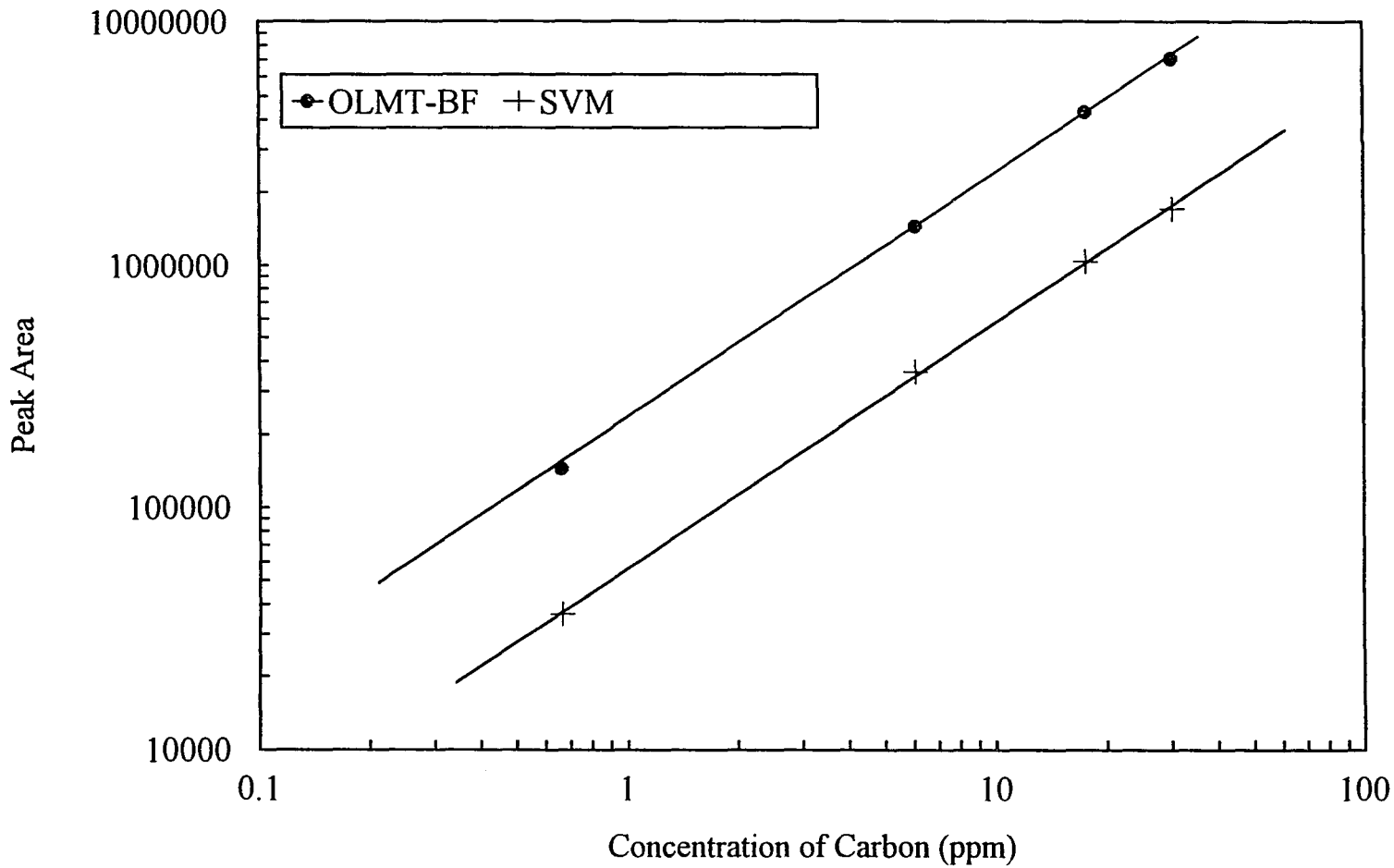


Figure 54 Calibration curve of NMOC using SVM and OLMT-BF systems.

The detection limit of the sequential valve microtrap NMOC system is dependent on the volume of sample loop. The larger the volume of the sample loop, the lower the detection limit since more sample was injected. But this is limited by the breakthrough volume of the particular sample. Furthermore, a longer injection time is required for large injection volume, so the injection frequency is limited. But the interval between two injections can not be very long since frequent injection is desired for continuous monitoring. The detection limit is evaluated as 2 ppb when the sample loop volume is 8 ml. For simultaneous valve microtrap NMOC system, flow rate of sampling and sampling time influence the detection limits. Again, the detection limits can not be further lowered by the increase of sampling volume because of the limitation of breakthrough volume. When sampling volume is 25 ml, the detection limit is 0.8 ppb.

6.3.2 Design of The Microtrap

The characteristics of microtrap can be described by the equations which describe a conventional sorbent trap. However, the microtrap operation is somewhat different from common sorbent trap, which are normally much larger in size and are seldom used in a continuous on-line monitoring. A common sorbent trap has 1/4 inch outer diameter and is 7 inches long. It has relatively large thermal mass so that it takes several minutes to make a thermal desorption. A microtrap is a short, small diameter tube packed with absorbent(s). A typical microtrap has 0.029 inch outer diameter, 0.021 inch inner diameter and 9 inch long. This microtrap can be heated or cooled very rapidly. The typical pulse time for thermal desorption is between 100 ms and 1000 ms [30]. This rapid heating can generate a "concentration pulse" which acts as a chromatographic injection.

However, the small diameter tubing can only be packed with a very limited amount of absorbent (around 30 mg). The breakthrough time and breakthrough volume are relatively small, specially for very light compounds such as methanol,

propane. In fact the microtrap is designed to trap sample only for 5~10 minutes when the sampling flow rate is at 3~8 ml/min.

Trapping efficiency (T) is one of major aspects which characterize the microtrap performance. The trapping efficiency of microtrap is defined as the fraction of the incoming sample retained by the microtrap before a injection is made [30]. The retention mechanism in a microtrap is an equilibrium between the concentration of sample in the stationary and mobile phase. The injections are normally made at fixed intervals of time. So trapping efficiency T:

$$T = \frac{t'}{t} \frac{k}{(1+k)} \tag{6.1}$$

Where t' is effective trapping time; t is the injection interval; k is capacity factor.

If injections are made very frequently such that t is less than breakthrough time t_b, the effective trapping time (t') is equal to t and above equation becomes:

$$T = k/(1+k) \tag{6.2}$$

Thus, in this case T, depends upon k, capacity factor and does not change with the injection interval t. When capacity factor k is greater than 20, the trapping efficiency is more than 95%.

If an injection interval, t, is large than t_b, the effective trapping time t' is equal to t_b. The trapping efficiency is inversely proportional to t and equation (6.1) becomes:

$$T = \frac{t_b}{t} \frac{k}{(1+k)} \tag{6.3}$$

According to the retention mechanism of microtrap, the retention time t_R can be described as following:

$$t_R = \frac{L}{\mu}(1+k) \tag{6.4}$$

Where L is the length of microtrap and μ is linear velocity of carrier gas.

Breakthrough time (t_b) is different from retention time (t_R) in the microtrap. In fact, the breakthrough time always is smaller than retention time. However, when a trap

has a enough high number of plates the breakthrough time is close to retention time [62]. The microtrap has about 100 theoretical plates when flow rate of carrier gas is about 4 ml/min. To simplify the equation, t_b replaces t_R in equation (6.4):

$$t_b = \frac{L}{\mu}(1+k) \tag{6.5}$$

Substituting equation (6.5) into equation (6.4), trapping efficiency at $t > t_b$ becomes:

$$T = \frac{Lk}{t\mu} \tag{6.6}$$

Therefore, in this case the trapping efficiency will be affected by the injection interval and the linear velocity of carrier gas.

A microtrap packed with Carbotrap™ C has low trapping efficiency for light and polar volatile organics such as propane and methanol since Carbotrap™ C has low surface area. To understand how long analytes stay in the microtrap, a certain amount of analyte was injected into the microtrap. Then after different delay times, a thermal desorption and an injection was made. The effect of delay time on trapping efficiency of various compounds by microtrap packed with Carbotrap™ C was shown in Figure 55. M-xylene can be trapped completely for about 25 minutes, but methanol is only trapped for 20 seconds. Although the previous work [60] has shown linear calibration curves can be obtained in both regions of interval ($t>t_b$ and $t<t_b$), a NMOC analyzer requires complete trapping to obtain an equal response for different species. Therefore the Carbotrap™ C microtrap is not suitable for widely varying NMOCs. However, Carbotrap™ C gives better desorption efficiency for heavy compounds such as dodecane. For the sequential valve microtrap NMOC system, the microtrap is designed for trapping organic compounds for 1 to 2 minutes. Therefore, it is suitable for most C_5 or higher compounds but is not good for very volatile compounds such as propane, methanol and dichloromethane.

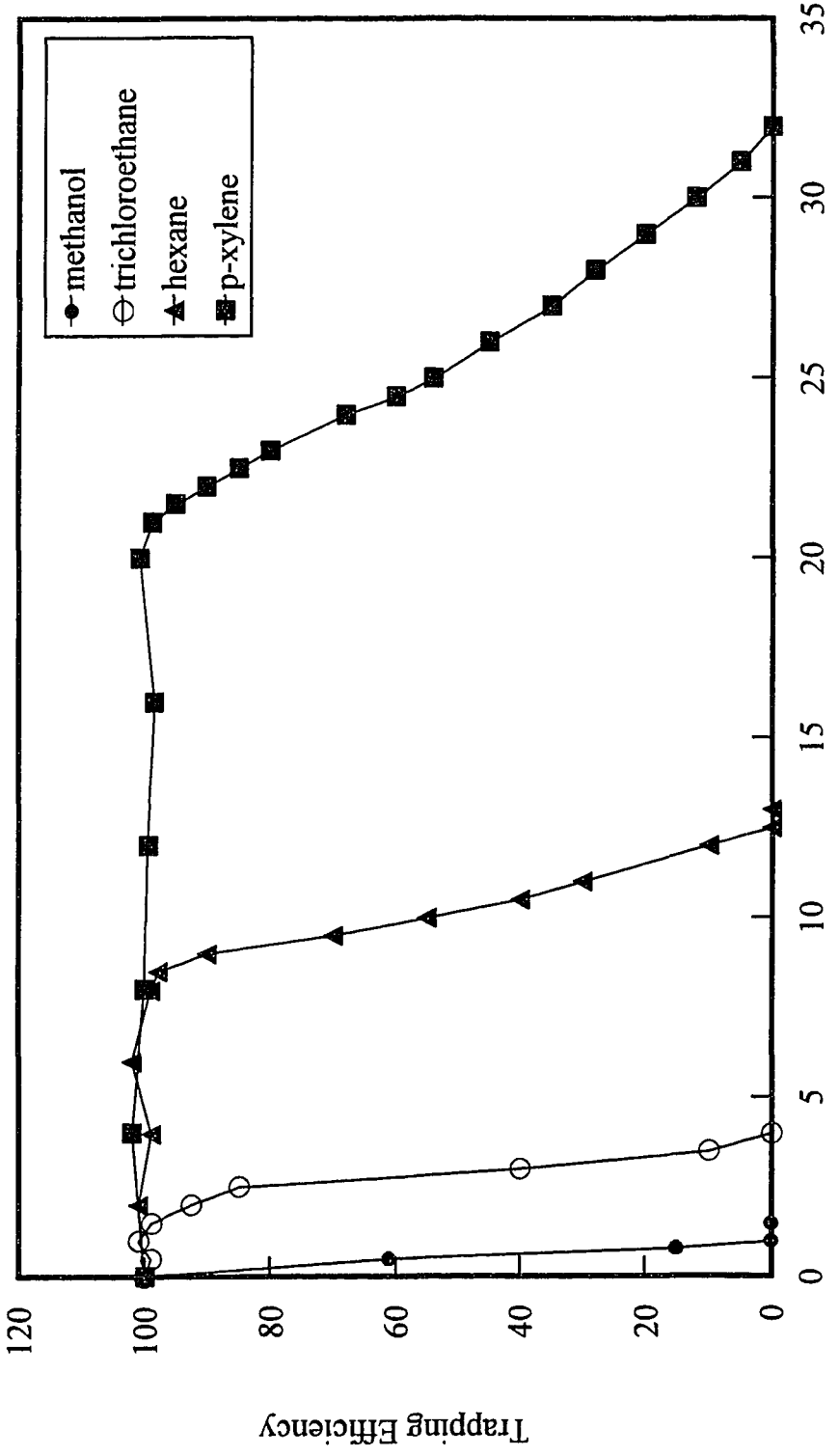


Figure 55 Effect of delay time on trapping efficiency in a microtrap packed with Carbotrap C. A 9 inch long 0.54 mm i.d. microtrap packed with Carbotrap C was used. The flow rate of carrier gas was 6 ml/min.

In fact, the injection interval may not be very short in practical application and every 5 to 10 minutes is suitable for making an injection. Therefore, to keep high trapping efficiency for very light compounds, the breakthrough time t_b has to be increased so that t_b is larger than interval time t. An adsorbent with high surface area can be used for light compounds. But heavy compounds are difficult to be desorbed in a single strong absorbent microtrap. Thus a multi-bed microtrap was developed which contained three adsorbents with different adsorption affinity to various VOCs.

In a multi-bed microtrap, several different types of absorbents were put a series of increasing absorbent affinity. The breakthrough time t_b can be expressed:

$$t_b = \sum t_i = \frac{L_1}{\mu}(1+k_1)+\frac{L_2}{\mu}(1+k_2)+\bullet\bullet\bullet+\frac{L_n}{\mu}(1+k_n) \qquad (6.7)$$

where $k_1<k_2<k_3 \cdots k_n$; $\sum L_i = L$.

In the multibed microtrap, Carbotrap™ C and Carbotrap™ B and Carbosieve™ S-III were put in series. At the sampling end of the trap, Carbotrap™ C is packed. A backflushing thermal desorption was used. Thus, when a sample stream which contains a variety of organic compounds passes through a multi-bed microtrap, the heavy compounds will be trapped by Carbotrap™ C and light compounds would break through from Carbotrap™ C. But they will be retained by Carbotrap™ B and Carbosieve™ S-III which have higher surface area. So the breakthrough time of light compounds in the multibed microtrap is much larger than that in a single bed (Carbotrap™ C) microtrap. In Figure 56, we can observe even for very light compounds such as methanol, acetone and MEK, the trapping efficiency remains almost 100% over 20 minutes, which is enough for general applications.

Desorption is also crucial aspect of a microtrap. When the microtrap was packed with Carbotrap™ C and Carbotrap™ (B), different compounds require

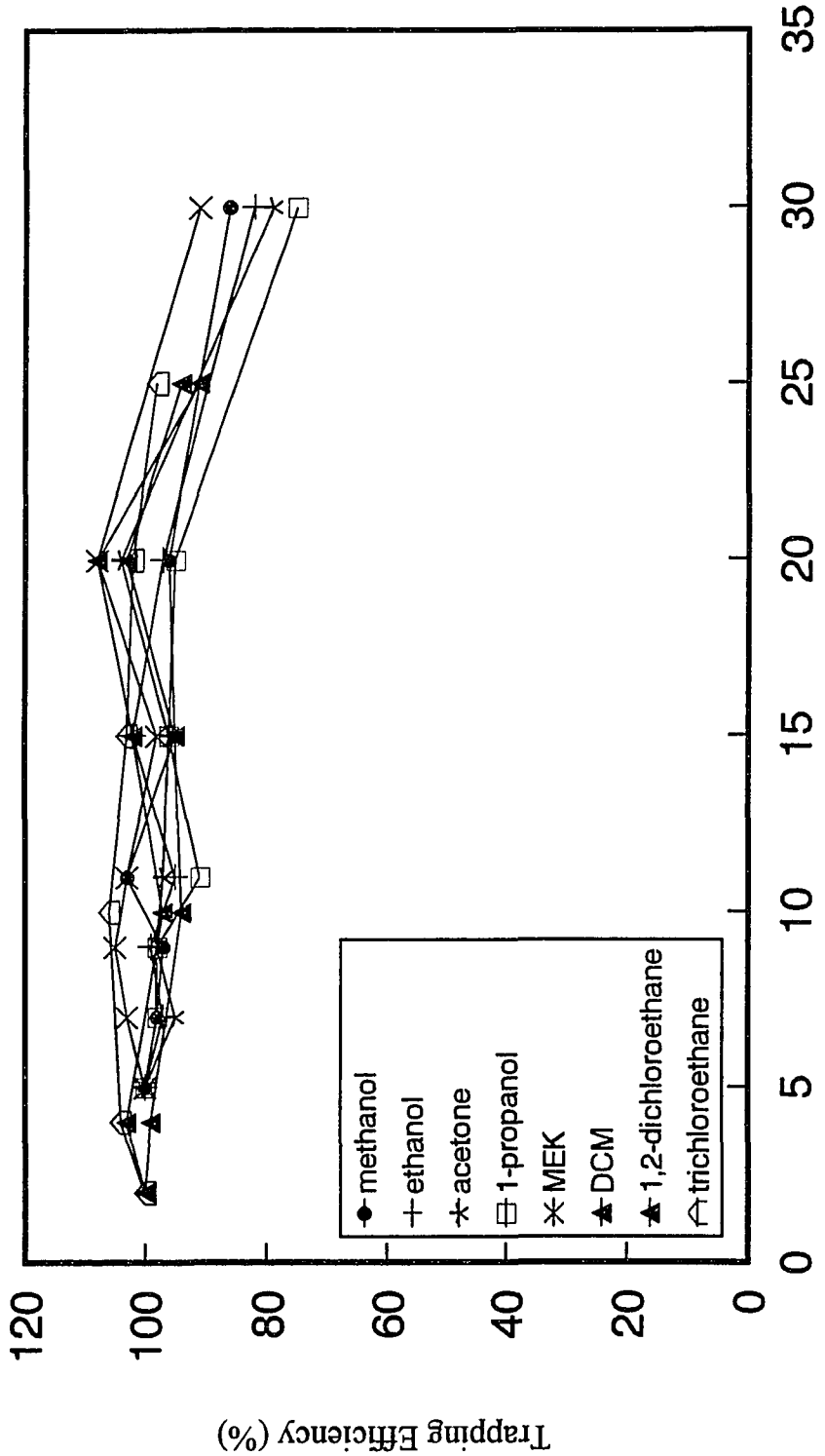


Figure 56 Effect of delay time on trapping efficiency in the multibed microtrap. A 6 inch 0.90 mm i.d. microtrap packed with Carbotrap C, Carbotrap and Carbosieve S-III in series. The flow rate of carrier gas was 6 ml/min.

different heating times for total desorption from microtrap, when a heating pulse is applied. In Figure 57, the desorption of dodecane is not completed even when the pulse time is 10 seconds. However, when a backflushing desorption (opposite direction to sampling) was used, the thermal desorption is completed easily. Figure 58 shows the thermal desorption profile from the multibed microtrap packed with Carbotrap™ C, Carbotrap™ (B) and Carboseive™ S-III using backflushing desorption.

Basically, an NMOC analyzer must have an equal response for each carbon from C_2 to heavy compounds such dodecane. Standard gases of various organic compounds were used to test the adsorption and thermal desorption performance of multibed microtrap. The results are presented in Figure 59. In this experiment, a standard gas stream continuously flowed through the multibed microtrap system, which followed a GC column. After different sampling times, an injection was introduced to the column. When the sampling time is increased the response increases proportionally for these test compounds. It means the multibed microtrap is able to completely trap and release these compounds which range from propane to ethylbenzene in this experiment.

6.3.3 Permanent Gas Interference

Permanent gases such as carbon dioxide and methane always coexist in environmental samples. In incineration stack gas, the concentration of carbon dioxide and carbon monoxide is extremely high. Moreover, these carbon-containing permanent gases have response in NMOC system and would interfere the NMOC analysis.

Several tests of CO_2, CH_4 and CO retention in the multibed microtrap have been done by connecting microtrap to a thermal conductivity detector (TCD). When 0.5 ml of pure carbon-containing permanent gas was injected to microtrap, total carbon-containing gases break through the microtrap in 15 seconds. So, when

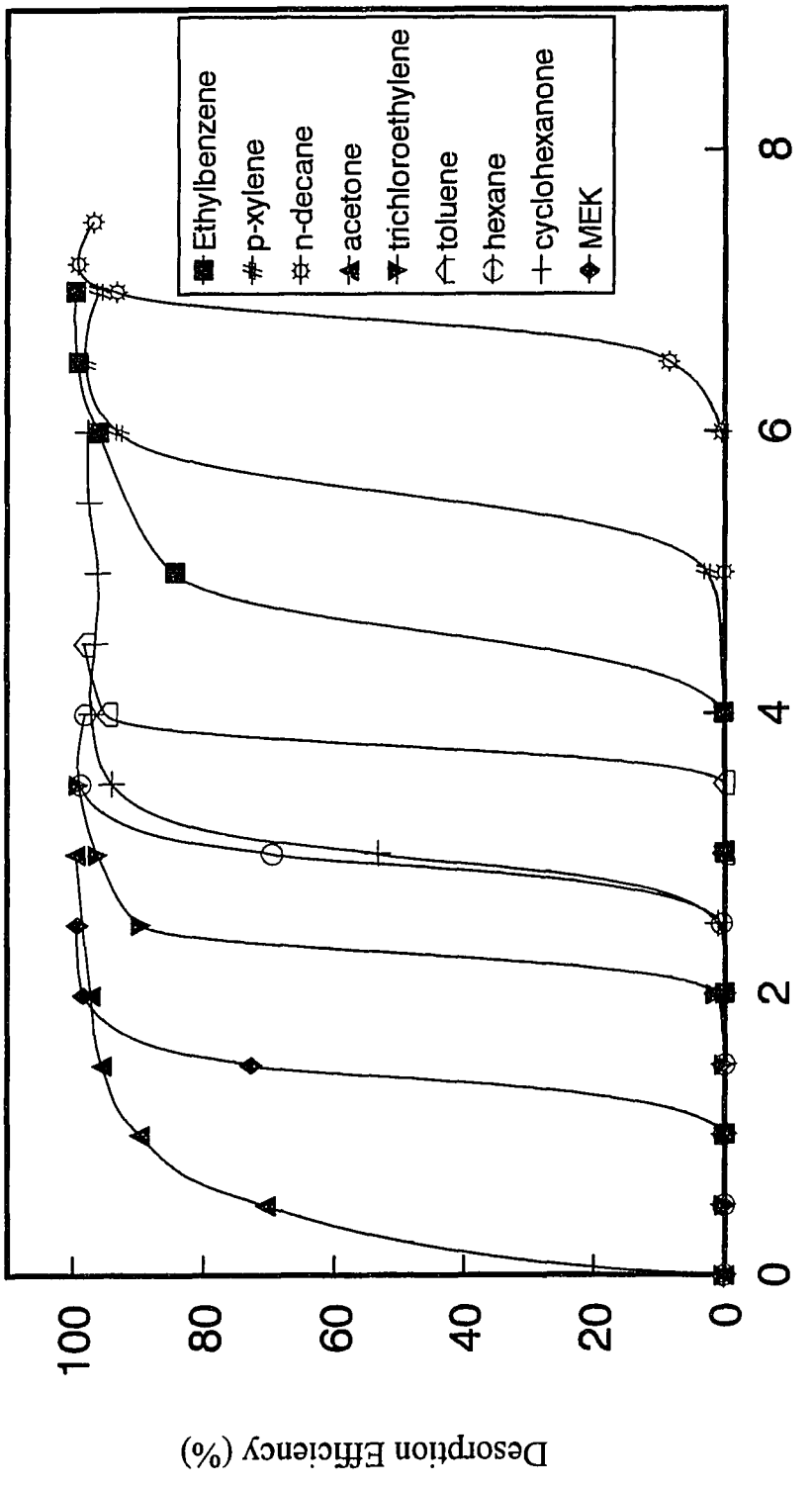


Figure 57 Desorption profile of the microtrap packed with Carbotrap C and Carbotrap (B) without backflushing. The current of electrical pulse was 25 A.

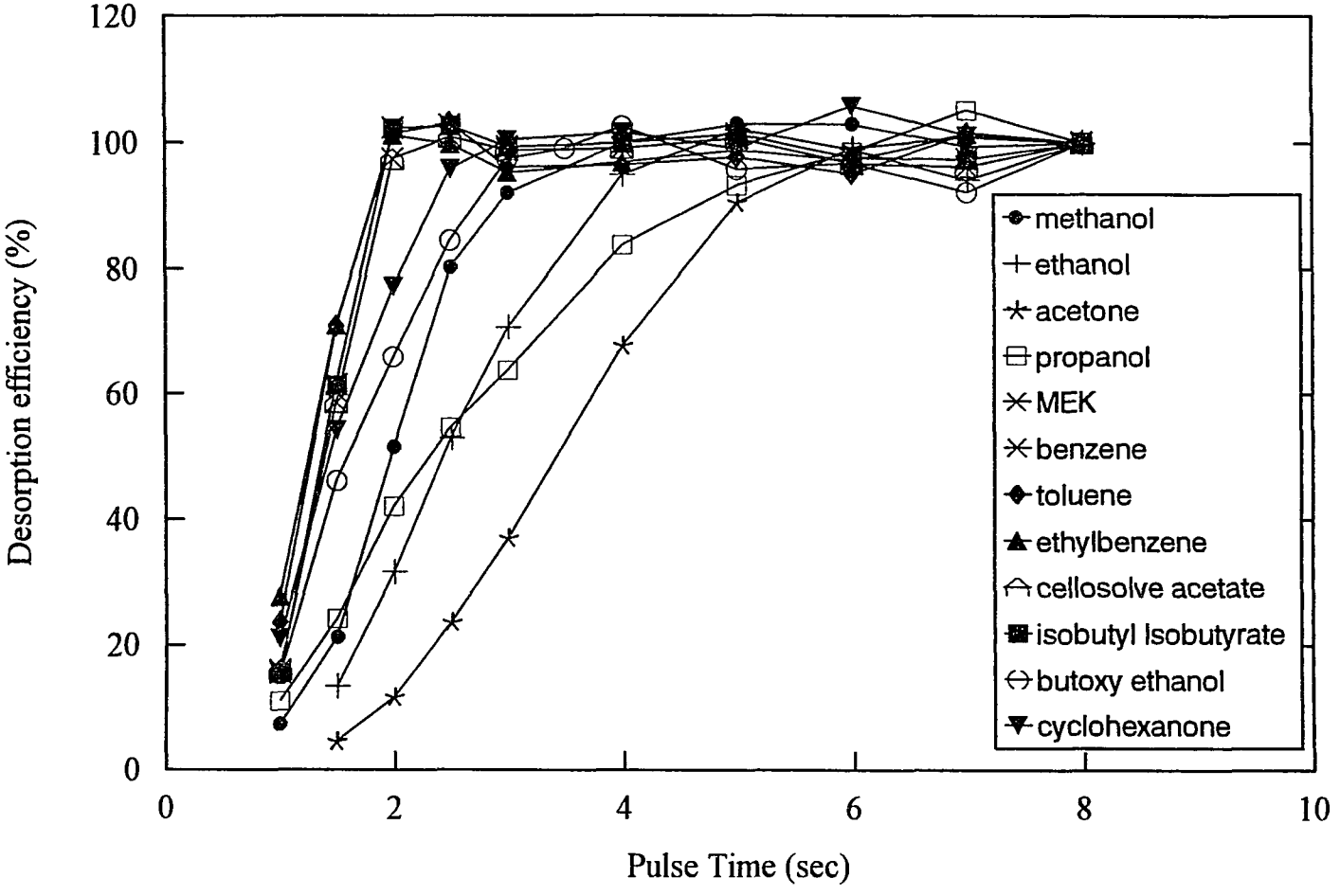


Figure 58 Desorption profile of VOCs from the multibed microtrap using backflushing technique. A 6 inch long 0.9 mm i.d. microtrap packed with Carbotrap C, Carbotrap (B) and Carbosieve S-III in series. The current of electrical pulse was 25 A.

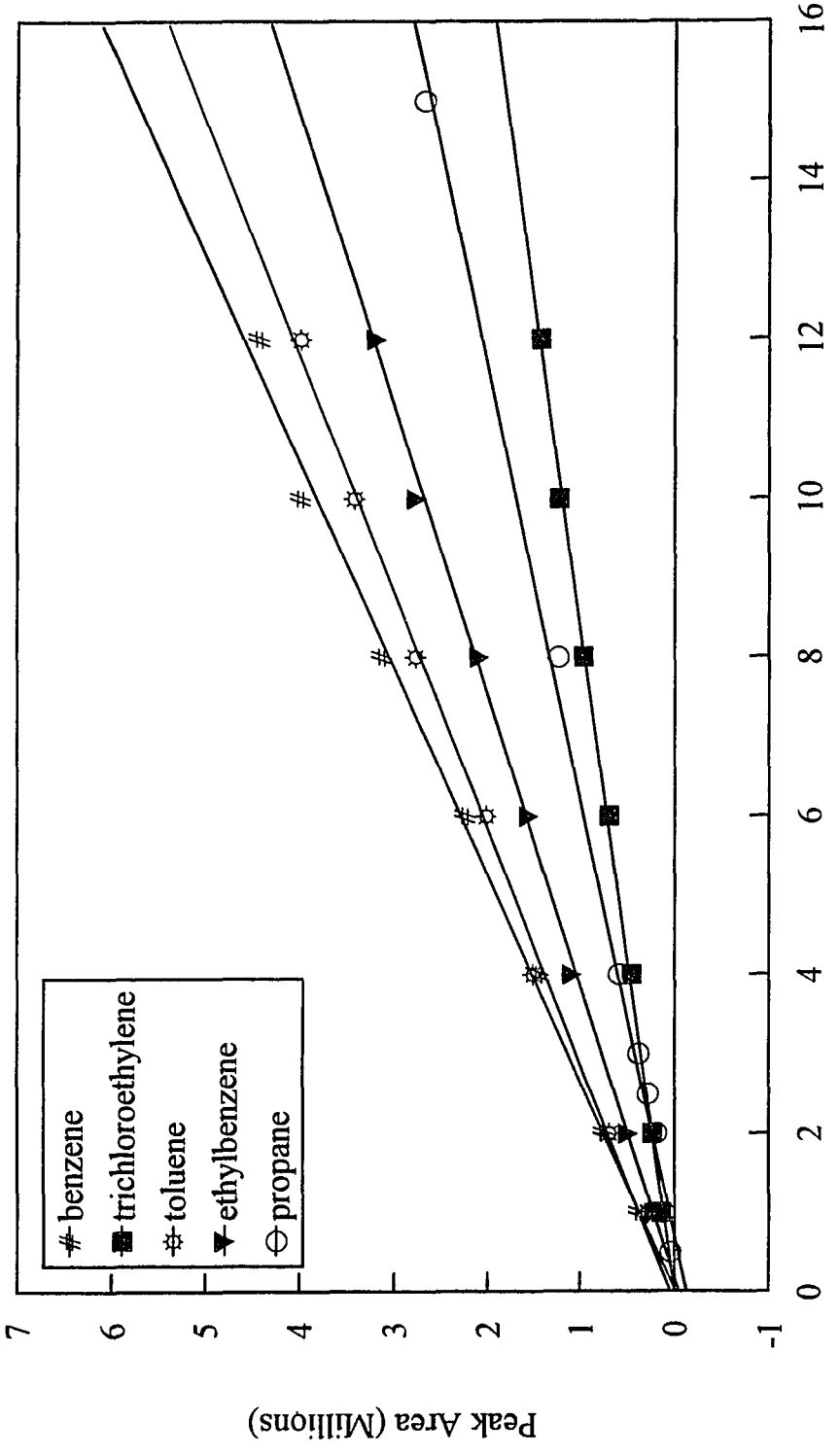


Figure 59 Response of analytical system as a fuction of sampling time. A 6 inch long 0.9 mm i.d. microtrap packed with Carbotrap C, Carbotrap (B) and Carbosieve S-III in series was used. The flow rate of sample stream was 6 ml/min.

the sample contained very high concentration of carbon-containing permanent gases was continuously flowed through microtrap, microtrap does not retain these gases. But these gases would flood the microtrap. However, these flooding carbon-containing permanent gases would be removed from system by purging the microtrap with an inert gas such as helium. In practical operation, it is required that the microtrap be purged with helium for about 20 ~ 60 seconds to remove carbon-containing permanent gas from the analytical system before injection.

Moisture content in environmental samples may vary from several ppm to 300 RH (relative humidity). High moisture content in a sample would affect the separation ability of column in EPA method 25. Carbotrap™ C, Carbotrap™ (B) and Carboseive™ S-III are hydrophobic adsorbents and have very small affinity for moisture [114]. Therefore, the NMOC peak area remains almost constant with increasing the moisture content in the sample (Figure 60).

6.4 Summary

Microtrap-based injection NMOC systems are able to continuously monitor NMOC in stack gas from incineration. The microtrap not only serves an automatic injector for NMOC analyzer but also a preconcentrator. The detection limit for this NMOC system is at low ppb level which is much lower than other conventional methods. This NMOC system can operate well even when samples contain high concentrations of carbon dioxide and moisture. Real sample tests in other studies [122] from Dr. Mitra's group have also demonstrated that the microtrap based NMOC analyzer worked very well in continuous monitoring of exhaust gas from a catalytic incinerator.

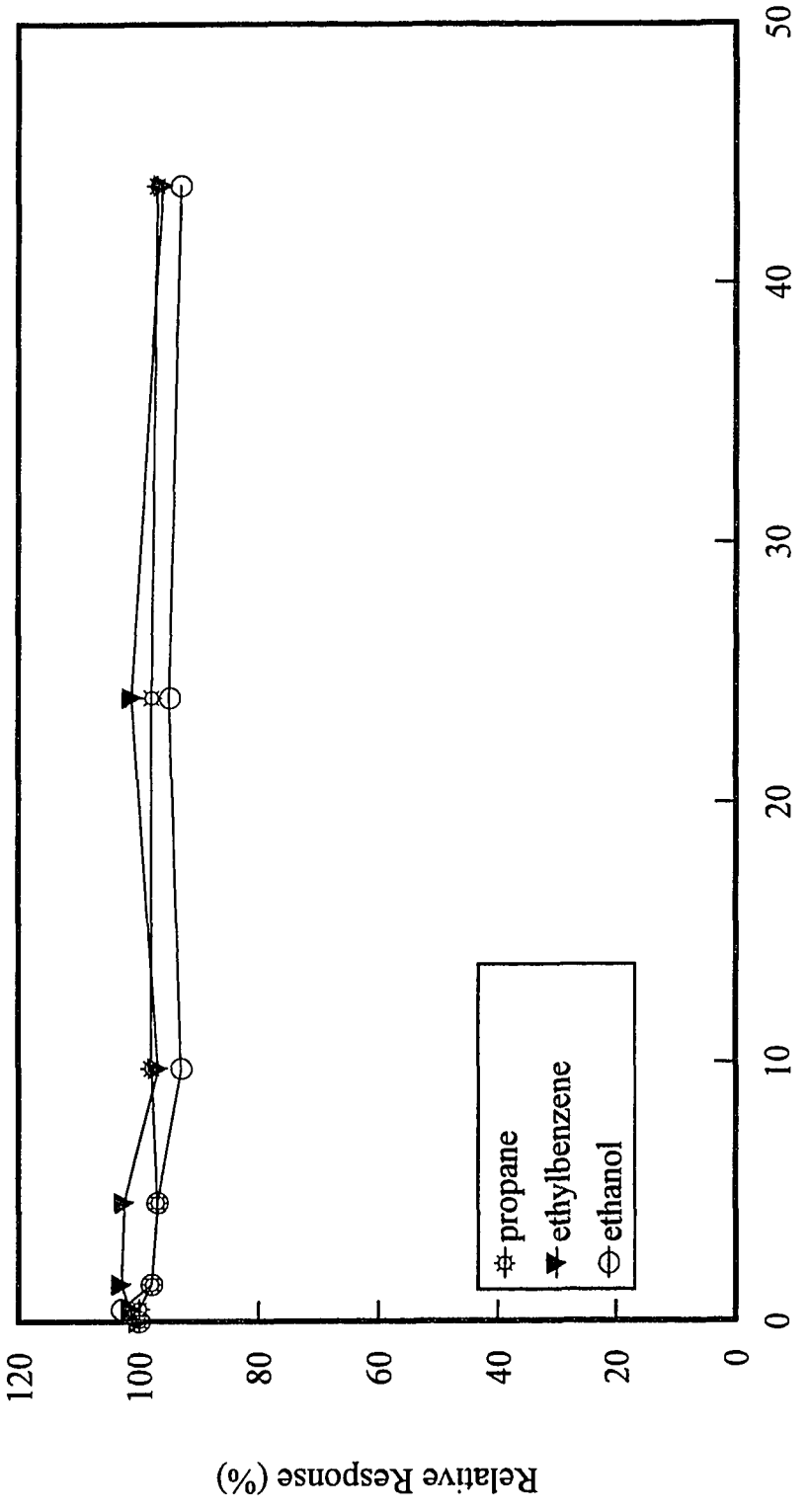


Figure 60 System response as a function of moisture concentration. The inlet concentration of NMOC was around 5 ppm.

CHAPTER 7

EVALUATION OF CANISTER-MINITRAP SYSTEM FOR SAMPLING AND ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR

7.1 Background

The quantitation of volatile organic compounds (VOCs) in ambient and indoor air is receiving more attention. VOCs are widespread in most industries as well as domestic use. VOCs are a group of pollutants that contain aromatic, oxygenated, chlorinated compounds. Many of them are toxic, and may be carcinogenic, or mutagenic at even very low concentrations in air. VOCs can react with NO_x under sunlight to form smog and ozone, which are even harmful to human health. The detection of these pollutants in air is of considerable importance since information on the concentration of VOCs in ambient air provides measures of the overall quality of the atmosphere and evaluation of smog and ozone formation potential.

Several approaches have been published for collection and analysis of VOCs in air [75, 116]. The methods for collection of air sample can be placed in two categories. Whole air samples have been taken in flexible, inert bags, glass bulbs, or Summa canisters [117, 118]. These grab samples are either analyzed directly, or are concentrated cryogenically before being injected into the gas chromatograph. The second category of technique combines the collection and concentration steps in the field, by selectively trapping the organic compounds on a solid sorbent [37, 119] The VOCs are recovered from the sorbent by extraction with solvent or by thermal desorption with a purge of inert gas. Table 8 lists the major advantages and disadvantages of each of these collection methods.

Collecting air sample in a Summa canister is one of the best methods since it results in fewer problems of compound-dependent recovery and less contamination. The advantage of Summa canisters is that the analysis of the sample can be repeated by using the remainder of the sample in the canister. In

contrast, the analysis of Tenax tubes by EPA Method TO-1 [120] allows for only one sample run because the whole sample is thermally desorbed at one time. In the circumstances where high levels of target compounds exceed the calibration range of the instrument, or should there be other problems with the instrumentation during the initial analysis, the sample would be lost. Finally, moisture, which frequently affects the trapping and desorption efficiency of the absorbent tubes (e.g., charcoal tubes), has no effect upon the canisters, assuming that no condensation occurs.

Table 8 Methods for Collection of VOCs in Air

Method of Sampling	Major Advantage	Major Disadvantage
Summa Canister	• Good sample recovery. • Rugged. • Can be thoroughly cleaned • Can be pressurized to increase sample volume • More than one analysis can be done.	• Limited sample volume • expensive • Further concentration is needed for trace analysis in most of application
Bags (Teflon, Tedlar etc.)	• Allows collection of 10 to 100 L sample • More than one analysis can be done.	• Difficult to clean • Fragile • Sample loss and contaminate influx through permeation
Glass Bulbs	• Can be thoroughly cleaned • Good sample recovery	• Limited sample volume • Fragile
Sorbent Trap	• Simple and convenient for sampling and transport • One step for collection and enrichment	• Sample volume limited by breakthrough volume • Contamination and sorbent bleeding • Compound-dependent recovery • Only one analysis can be done

After sample collection, gas chromatography is commonly used to detect and quantitate the VOCs in air sample. Direct injection can be used for high concentration samples. However, in most cases, a concentration step is necessary since the concentration of VOCs in ambient air is very low (ppb_v). A cryogenic trap is generally used to preconcentrate the VOCs in ambient air. A common cryogenic trap is a metal tube packed with silanized glass beads. A steady stream

of cryogenic fluid such as liquid nitrogen is used to make the trap temperature sufficiently low to quantitatively collect all sample components of interest. With temperatures in the range of -100°C to -125 °C, all organic compounds less volatile than pentane can be trapped. After the sample is preconcentrated, a current pulse from a capacity discharge power supply is used to heat the metal tube. The VOCs can be released readily when heating the metal tube since it was packed only with glass beads. Thus a narrow sample plug can be generated and injected into the GC column.

The cryogenic trap is very useful for routine air analysis. However, it has some limitations. First of all, the sampling volume of air sample is limited because of problems associated with the collection of water vapor. The frozen water ice can block the path of the gas flow. Liquid nitrogen is also expensive and inconvenient.

A sorbent trap such as Tenax may also be used to collect the organic vapors from the air sample from canister. Basically Tenax is a hydrophobic sorbent and eliminates the collection of excess water. This type of sorbent trap has been proven to efficiently adsorb a large number of VOCs and release them at 180 °C. The desorption time is usually about 3 minutes. The released sample is swept onto the chromatographic column by purging carrier gas through the heated trap. However, the released sample can not be directly introduced into capillary column since the desorption is not rapid enough to serve as an injection. To obtain a good separation, a cryogenic trap or a sub-ambient initial column temperature is needed to refocus the sample into a sharp "concentrated pulse" at the column head. Thus the analytical system becomes more complicated and the cost of analysis is increased.

Microtraps have been used to continuously monitor the VOCs in air stream [30, 31]. A microtrap is a small diameter tube packed with an adsorbent such as Carbotrap C. It has been shown to preconcentrate the sample and thermally desorb

the VOCs in a second. The desorbed sample can directly injected into GC column. However, the sample volume is limited and some of the VOCs may break through in a minute. Thus the microtrap can not quantitatively trap most of the VOCs unless it is cooled to a sub-ambient temperature [30].

In the approach described here, a multi-bed minitrap, packed with Carbotrap C, Carbotrap (B) and Carbosieve S-III in series, was developed as an interface between the GC and the canister. It was applied to the determination of the VOCs at trace levels in ambient air. In this analytical system, the minitrap replaces the sample loop in a six port valve placed in front of the GC column. When a vacuum pump draws the air sample from the canister through the minitrap, the organic vapors are selectively trapped. The trapping efficiency is improved since three different adsorbents were packed in the minitrap. Desorption also become much easier since the thermal mass of minitrap is so small that it is easily heated. Thus, the desorbed sample can be directly introduced into GC column as an injection, without any refocusing.

7.2 Experimental

7.2.1 Reagent and Materials

Adsorbents such Carbotrap C, Carbotrap (B) and Carbosieve S-III were supplied by Supelco Company (Bellefonte, PA). All the organic chemicals were chromatographic grade from Fisher Scientific. The standard gases came from AIRLIQUIDE Inc. (Morrisville, PA). One contains 2 ppm of toluene, 4.8 ppm of ethyl acrylate and 4.8 ppm of acrylonitrile and the other contains 5 ppm methanol, 3 ppm methylene chloride, 1.9 ppm ethyl acrylate, 2.0 ppm hexane, 2.1 ppm benzene, 2.0 ppm 1,1,1-trichloroethane, 2.0 ppm dichloropropane, 2.0 ppm dibromomethane, 4 ppm toluene, 2.1 ppm styrene, 2.0 ppm p-xylene, 2.0 ppm m-xylene, 2.0 ppm ethylbenzene, 2.0 ppm p-dichlorobenzene, 2.0 ppm m-dichlorobenzene, 1 ppm iso-propylbenzene, 2.0 ppm naphthalene and 2.0 ppm

trichlorobenzene. Canisters were supplied by Scientific Instrumentation Specialists (Moscow, ID).

7.2.2 Instrumentation

The schematic diagram of the experiment system is shown in Figure 61. A modified sampling valve in which sample loop is replaced with a minitrap is placed between canister and GC column. When the vacuum pump draws the air sample from canister, the sample flows through the multi-bed minitrap. The minitrap is a stainless steel tube which is 1.5 mm id x1.8 mm o. d. x 10 cm long. It was packed with 55 mg of 20/40 mesh Carbotrap™ C, 25 mg of Carbotrap™ (B) and 10 mg of Carbosieve™ S-III in series. Silanized glass wool was used to separate the adsorbents in the minitrap. After packing, the trap was attached to a manifold and put into GC oven at 300 °C for 24 hours with a purge of nitrogen flowing at 30 ml/min. Sampling direction was from Carbotrap™ C to Carbosieve™ S-III. Thus the heavy compounds in the sample are adsorbed by Carbotrap™ C. The less heavy compounds may break through the Carbotrap™ C and be collected by Carbotrap™ (B) or Carbosieve™ S-III. When desorbing, a backflushing technique was used with the purging gas flowing from Carbosieve™ S-III to Carbotrap™ C. The rapid heating needed for desorption was accomplished by passing an electrical current through the tube wall. The power supply was controlled by a timer.

Since the minitrap has very a small thermal mass the trap is easy to heat. Figure 62 presents a temperature profile of the minitrap. The temperature can rise to over 400 °C in 4 seconds. Such a high heating rate is beneficial to generate a "concentration pulse" which serves as injection. In this study, a 30 A current was used to heat the minitrap and the heating time was four seconds.

A Varian 3700 gas chromatograph (Varian, CA) equipped with a conventional flame ionization was used for analysis. APEX Chromatography

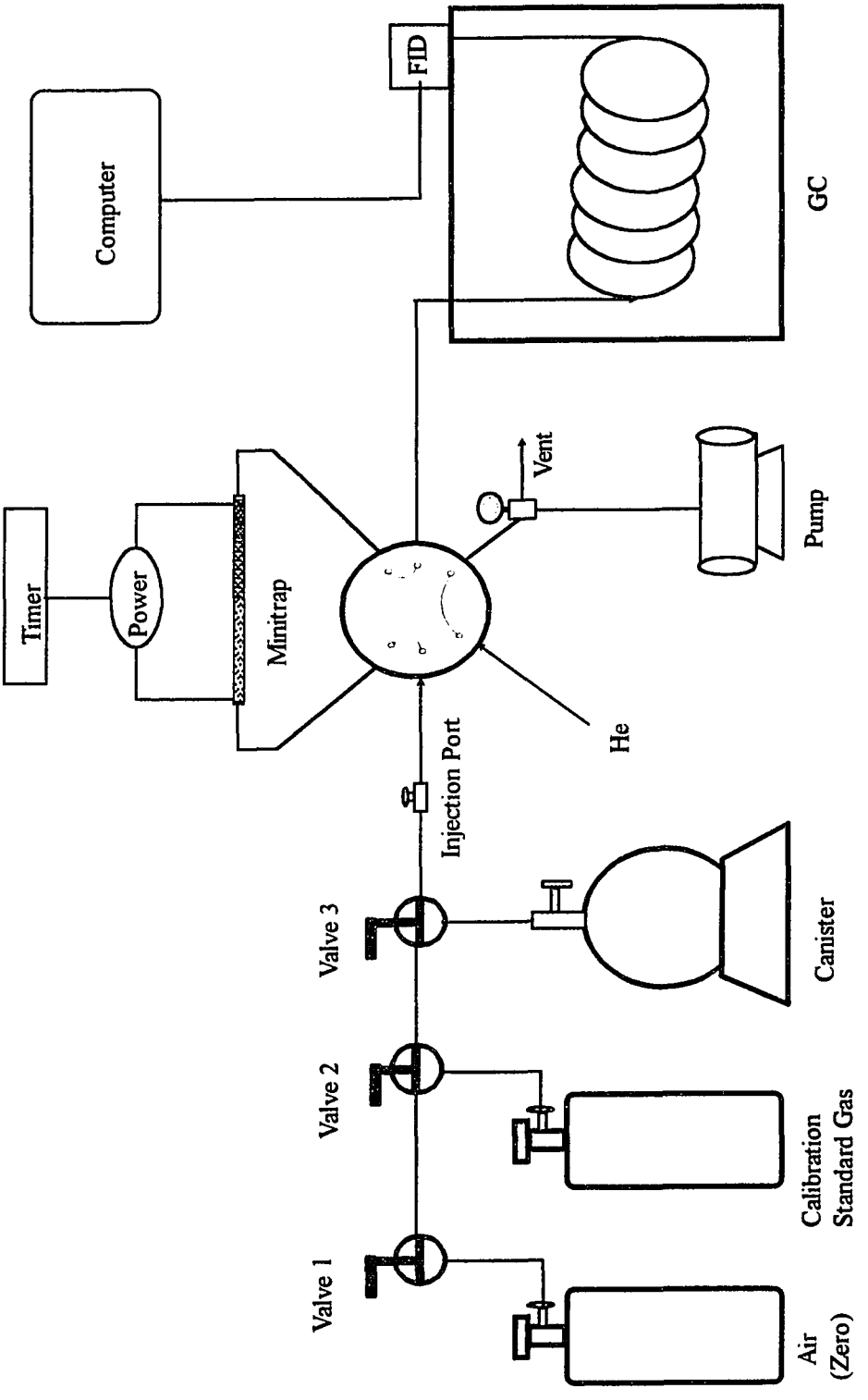


Figure 61 The canister-minitrap system for VOCs analysis in ambient air.

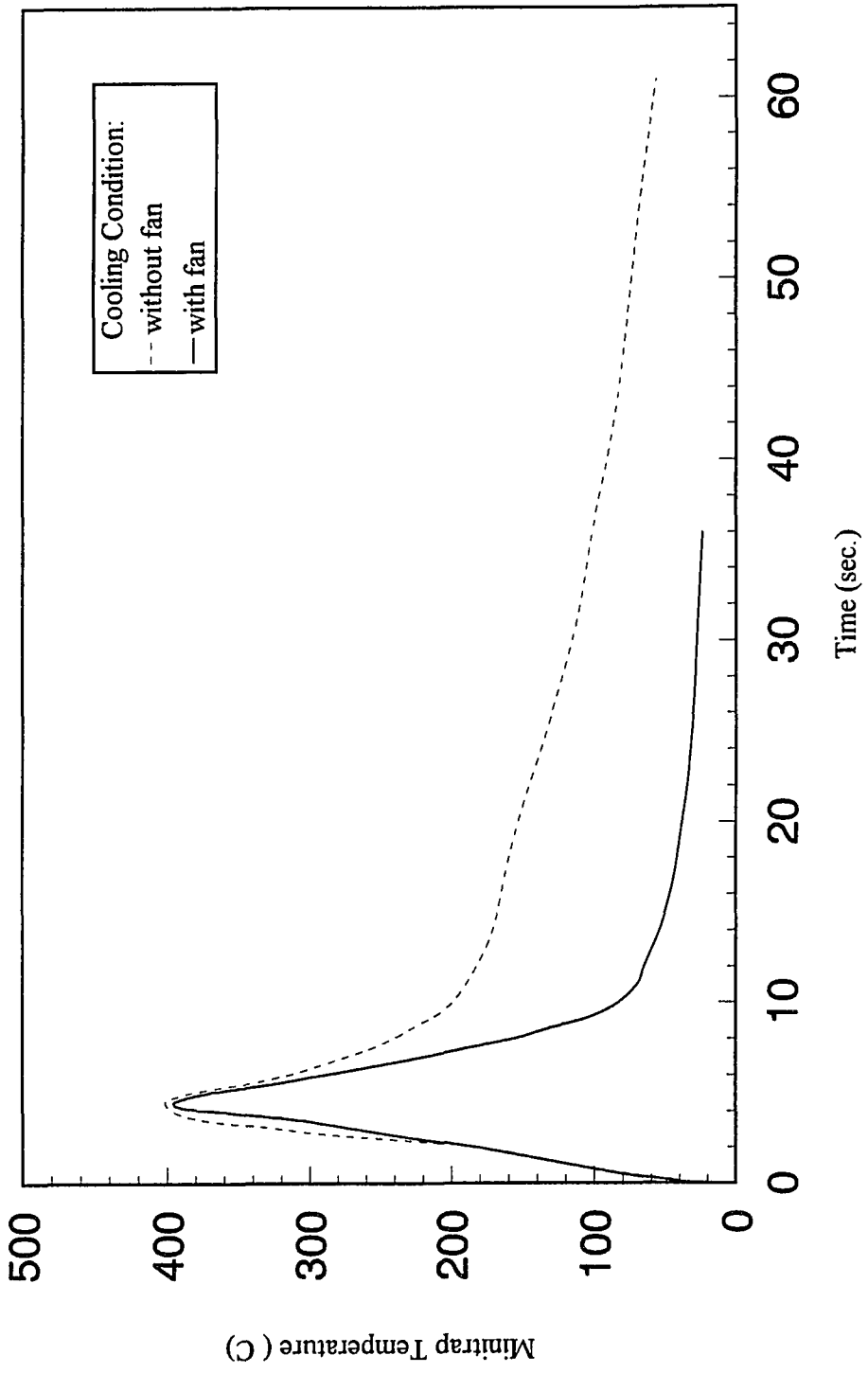


Figure 62 Minitrap temperature profile on heating-cooling cycle. The pulse current was 30 A and heating time was 4 seconds. A 10 cm long 1.5 mm i.d. minitrap was used.

workstation was used to acquire the data. A 30 m long SE-30 fused silica open tubular column from Alltech (Deerfield, IL) was used. The column inner diameter is 0.53 mm, and the thickness of stationary phase is 1.0 μm.

A lab-made standard gas was prepared in a 13-L stainless steel tank by injecting a known amount of pure liquid organic compounds and filling with dry zero air to 200 psi pressure. The concentration of VOCs in this standard gas was verified by comparison with the standard gas from AIRLIQUIDE (Morrisville, PA).

7.2.3 Operation of System

Before sampling, the canister was cleaned by evacuating and filling with dry zero air four times. During this period, the canister was heated to 100 °C with heating tape. Then the canister was evacuated to -30 psi and taken to the sampling site. The valve was opened to let the air sample into the canister and the ambient temperature was recorded. Then the canister valve was closed and it was taken to lab for analysis.

Before performing analysis, valve 1 was opened and the minitrap was purged with zero grade air or nitrogen and heated. After system was cleaned, valve 3 was opened and the vacuum was turned on. The sampling time and sampling flowrate were recorded. After sampling, the system was purged with dry air for about 3 minutes at 30 ml/min. Then the valve was switched to the injection position and the minitrap was pulsed for four seconds. The GC temperature program was started and the chromatogram was recorded.

For calibration, valve 2 was opened and the above steps were followed. All transfer lines were heated to 100 °C to prevent the adsorption of compounds of interest.

7.3 Results and Discussion

7.3.1 Trapping Efficiency of Minitrap

The list of VOCs contains various organic compounds from C_2 to C_{20}. Basically, an adsorbent has different affinities and the trapping efficiency varies from compound to compound. To overcome this problem, three adsorbents, Carbotrap™ C, Carbotrap™ (B) and Carbosieve™ S-III, were packed in series for the minitrap. These three adsorbents belong to Type I - nonspecific adsorbents [66] and are hydrophobic. Carbotrap™ C has the lowest surface area and is good for heavy compounds such C_8 or larger. Carbotrap™ (B) is designed for C_5~C_8 compounds. Carbosieve™ S-III has a very much larger surface area and can effectively trap very volatile compounds such as methylene chloride and vinyl chloride [121]. When an air sample stream flows through the minitrap, the heavy compounds in the sample are trapped by Carbotrap™ C. Light compounds may break through the Carbotrap™ C segment but these all are collected by Carbotrap™ (B) or Carbosieve™ S-III.

The trapping efficiency has been studied in a series of experiments. A stream of zero grade air is passed through the minitrap by pumping air from a canister at a rate of 10 to 20 ml/min. At the beginning, an 1 ml portion of lab-made standard gas mixture is injected into the stream. When the sampling volume reaches 1000 milliliters, 60 ml of dry zero grade air was passed through the minitrap at 20 ml /ml to remove retained moisture. Then the system was switched to injection mode. An electrical pulse was applied to the minitrap and the released VOCs were injected into GC. The amounts of analyte recovered were compared with amounts obtained by sample valve analysis of standard gas. The sampling efficiency is calculated as follows:

$$\text{Trapping efficiency} = \frac{\text{amounts recovered by minitrap}}{\text{amounts obtained by valve analysis}} \bullet \frac{\text{volume of sample loop(ml)}}{1}$$

Table 9 shows the trapping efficiency of some typical VOCs at 1000 milliliters of sampling volume. The data in Table 9 is the average of three replicate analyses. The trapping efficiency of the minitrap for the tested compounds is close to 100%.

Table 9 Trapping Efficiency of Minitrap[1]

Compound	Trapping Efficiency (%)	Relative Standard Deviation (%) (n=3)
Acetone	110	17.1
Methylene Chloride	105	16.8
Butanol-1	95	6.9
Benzene	102	2.8
1,1,1-trichloroethane	92	3.9
Chlorobenzene	108	4.1
O-xylene	93	3.2
Dodecane	89	4.5

1. The concentration of standard gas mixture was about 1 ppm_v. The volume of sample loop is 0.5 ml. The pulse time was 4 seconds and electrical current was 30 A.

7.3.2 Desorption Efficiency

The minitrap is a small diameter tube and has a very thin wall. Thus it has a small thermal mass and can be heated very rapidly. In Figure 62 we can see that the minitrap temperature reaches 400 °C in 4 seconds. On the other hand, unlike Tenax adsorbent which has maximum desorption temperature of 280 °C, carbon black adsorbents can resist much higher temperatures. The maximum desorption temperature is above 400 °C. When a higher desorption temperature is used, the desorption time can be reduced. In this study the desorption time was 4 seconds. Thus a "concentrated pulse" can be generated and can serve as a GC injection without any cryofocus device. Figure 63 presents the relationship between

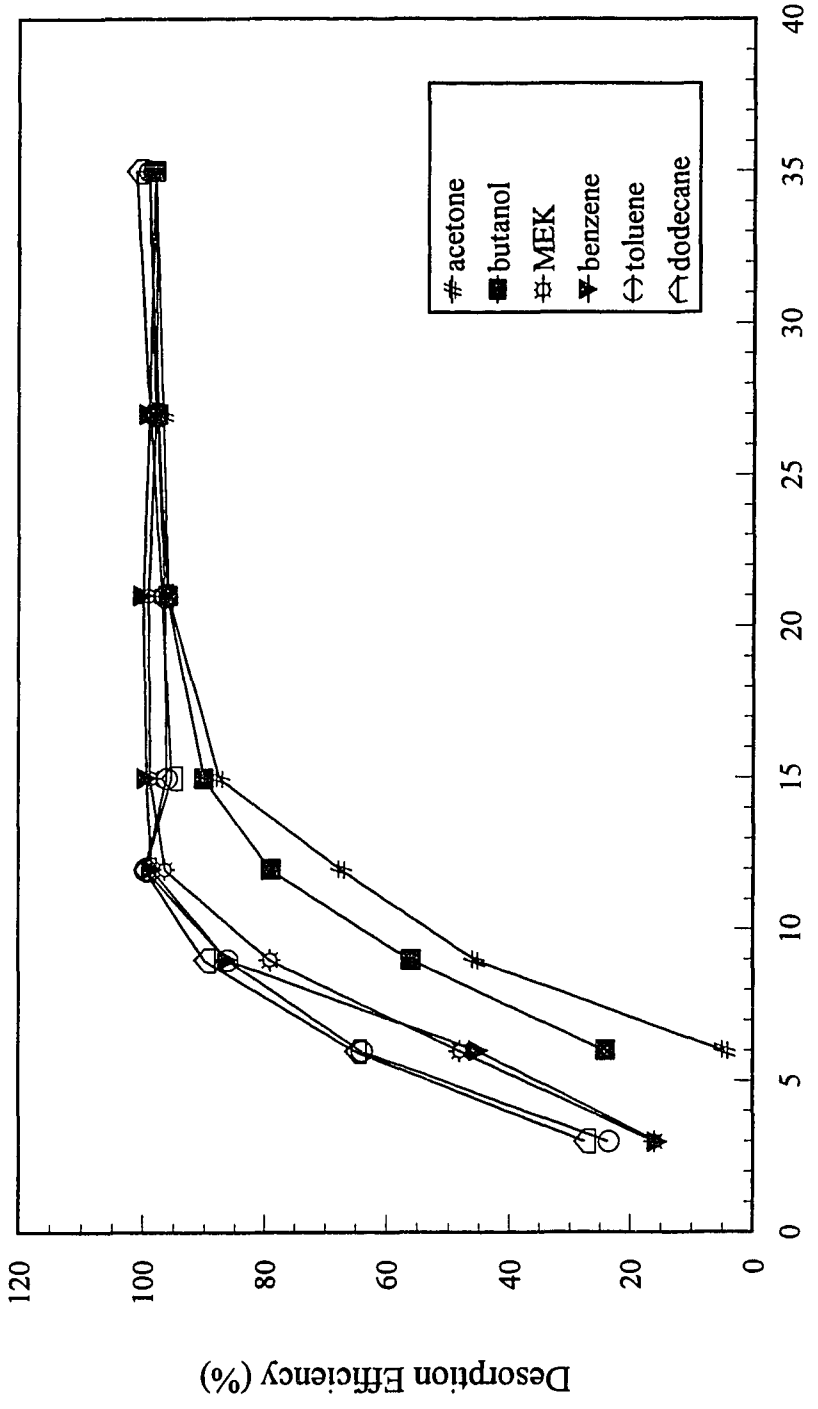


Figure 63 Relationship between desorption efficiency and heating current. The concentration of tested compounds was about 1 ppm. The sampling volume was 200 ml and the heating time was 4 seconds.

desorption efficiency and the heating current. The desorption efficiency was calculated by:

$$\text{Desorption efficiency (\%)} = \frac{\text{amount found in the first desorption}}{\text{total amount found in three successive desorptions}} \bullet 100$$

The desorption efficiency in Figure 63 was obtained by averaging three tests. The desorption was found to be quantitative when a pulse current of 21 A or larger was used for these compounds.

The rate of desorption and of sample injection depends mainly on maximum temperature achievable and the heating rate. The completeness of the desorption can be improved with increasing pulse energy. The pulse energy is a function of pulse time and pulse current. Figure 64 presents the relationship between desorption efficiency and pulse energy without backflushing. It is seen that heavy compounds require long pulse time when without backflushing technique. Desorption is much easier when using backflushing technique.

On the other hand, increasing pulse energy increases the heating rate and the maximum desorption temperature. Figure 65 shows the results of improvement of column resolution by increasing pulse energy. However, some oxygenated VOCs such as acetone, and methylethylketone may be decomposed in the sorbent trap if too high a desorption temperature and too a long heating time are used. Mangani et. al [122] found that a longer heating time plays a more important role in the possibility of decomposition than higher desorption temperature. Fortunately, the pulse time required for minitrap is only 4 seconds which more than 20 times less than that for a common sorbent trap. No decomposition occurs for any of the compounds tested in this study. Figure 66 shows a example of GC chromatograms using different desorption times. Since the two chromatograms show no difference, it can be concluded that a four seconds desorption time is adequate for total desorption and a longer desorption time is unnecessary.

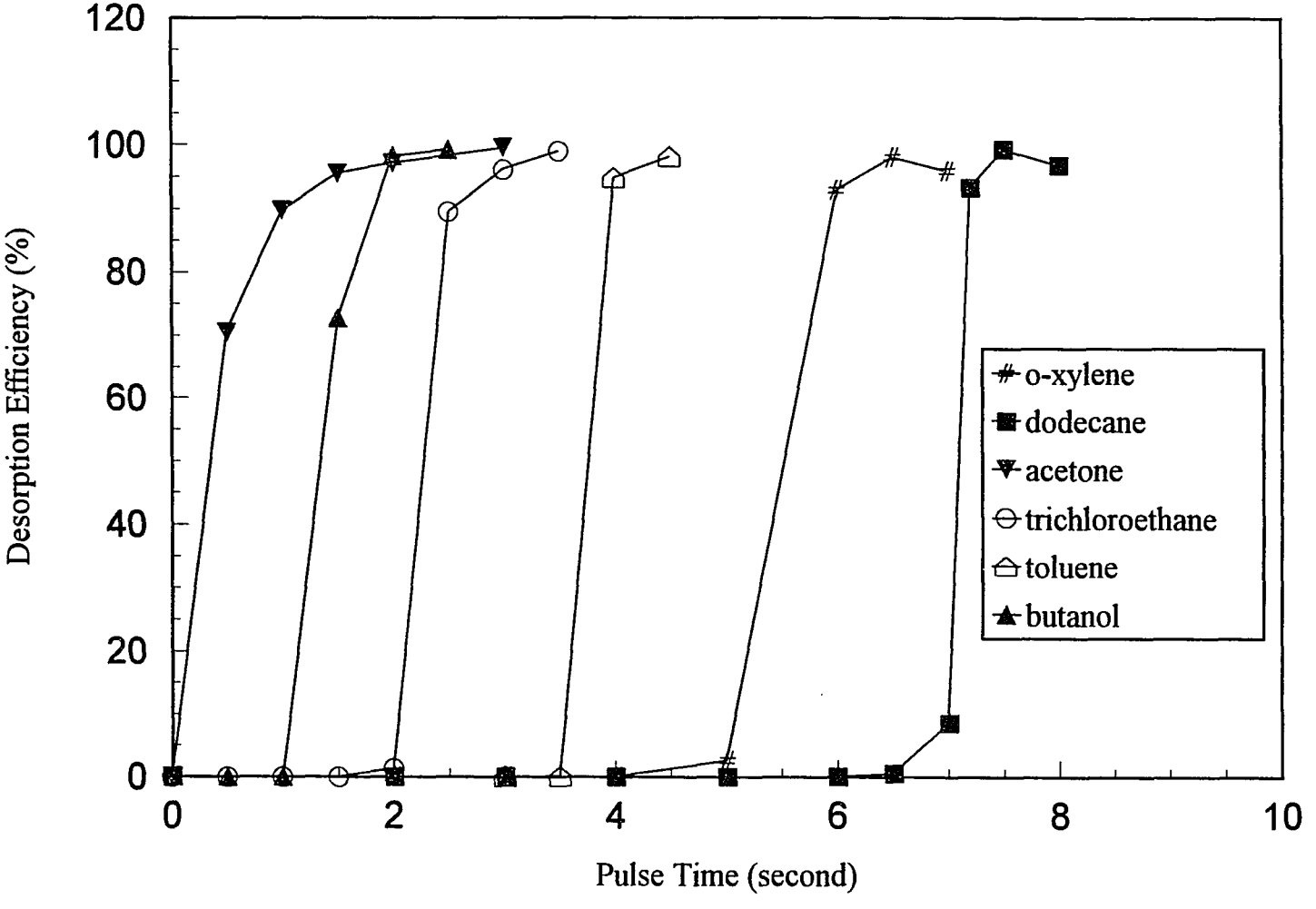


Figure 64 Effect of pulse time on desorption efficiency. The minitrap was packed with Carbotrap C and Carbotrap (B). 20 A current was used to desorb without backflushing technique.

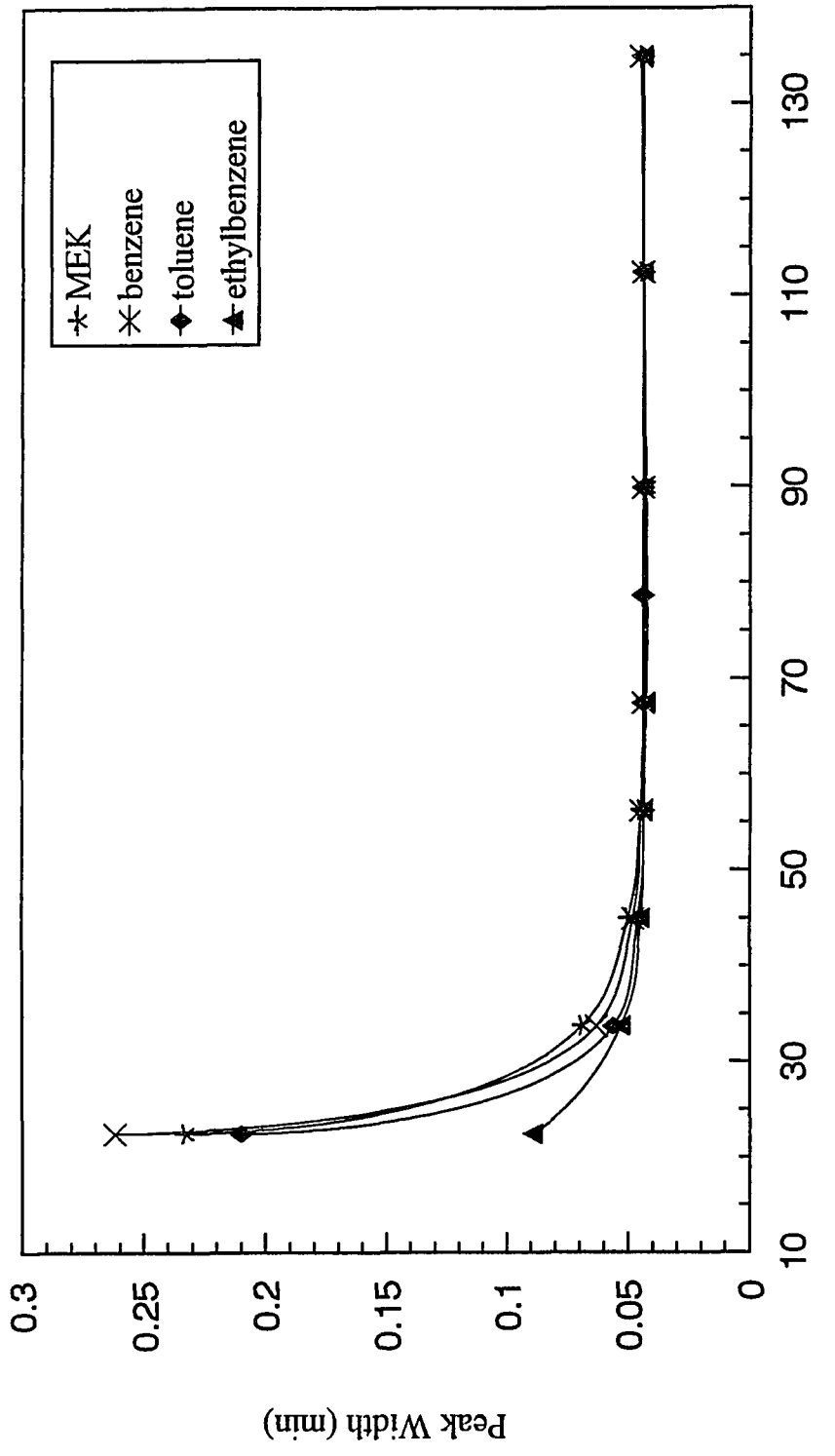


Figure 65 Effect of pulse energy on peak width. A 10 cm long 0.72 mm i.d. minitrap was used and the pulse current was 15 A. The pulse energy was calculated by A^2 x R x T.

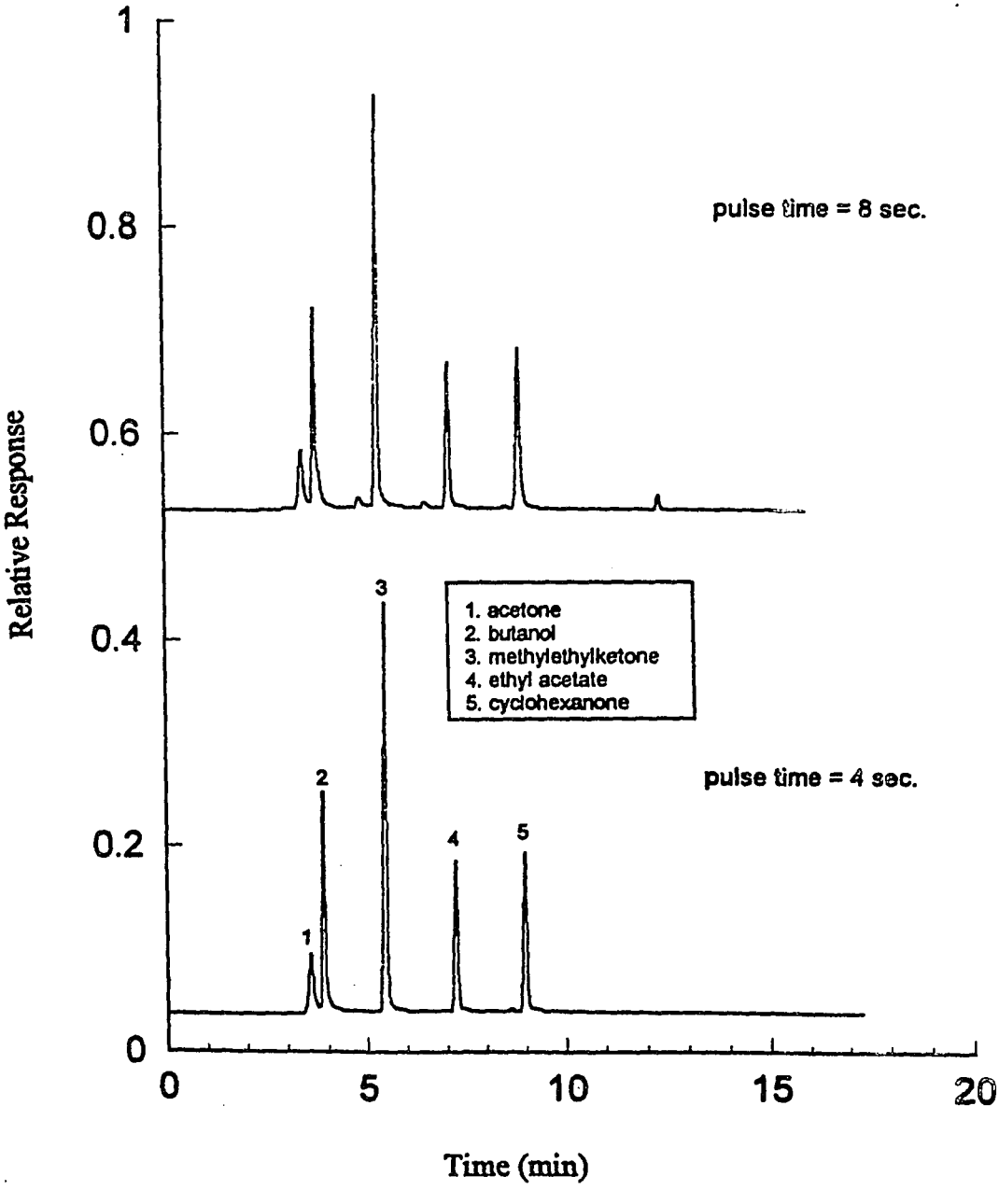


Figure 66 Chromatograms of VOCs at different pulse duration. A 10 cm long 1.5 mm i.d. multibed packed with Carbotrap C, Carbotrap B and Carbosieve S-III was used. The pulse current was 30A.

However, if a longer desorption time is needed in a special case, no decomposition will occur for oxygenated compounds.

In this analytical system, the desorption temperature for minitrap is approximately 400 °C. The thermal stability of the adsorbents packed in the minitrap must be considered. However, no significant degradation of performance has been observed after 200 pulses were applied to a minitrap.

7.3.3 Effect of Sampling Volume and Moisture Effect

The concentration of VOCs in ambient air is very low (ppb level) in most cases. The larger the volume of air is sampled, the better for quantitation. However, the sampling volume is limited by the volume of canister and the breakthrough of target compounds from minitrap. The volume of the most common canister is six liters which is enough for most applications. The evaluation of VOCs breakthrough from the minitrap was achieved by increasing the sampling time at 20 ml/min. Figure 67 presents the relationship between peak area and sampling time or volume. In this experiment, the concentration of analytes was about 1 ppm. For light compounds such as acetone, methylene chloride and 1- butanol, the curve is linear until the sample volume exceeded 1500 ml. For xylene, dodecane and other heavy compounds, the sampling volume can reach 2500 liter before they break through. However, the breakthrough volume is affected by the concentration of analyte [62, 63]. Bertoni et. al [63] found that the breakthrough volume was increased with decrease of concentration of analyte in air. Thus for ppb level analysis, the breakthrough volume can be much larger than that obtained in this test. However, to ensure no breakthrough occurs during sampling, it is safe to take up to 1200 ml sampling volume in this system.

In a cryogenic trap system, the sampling volume is limited by the moisture since the water vapor freezes and blocks the sample flow. In the canister-minitrap

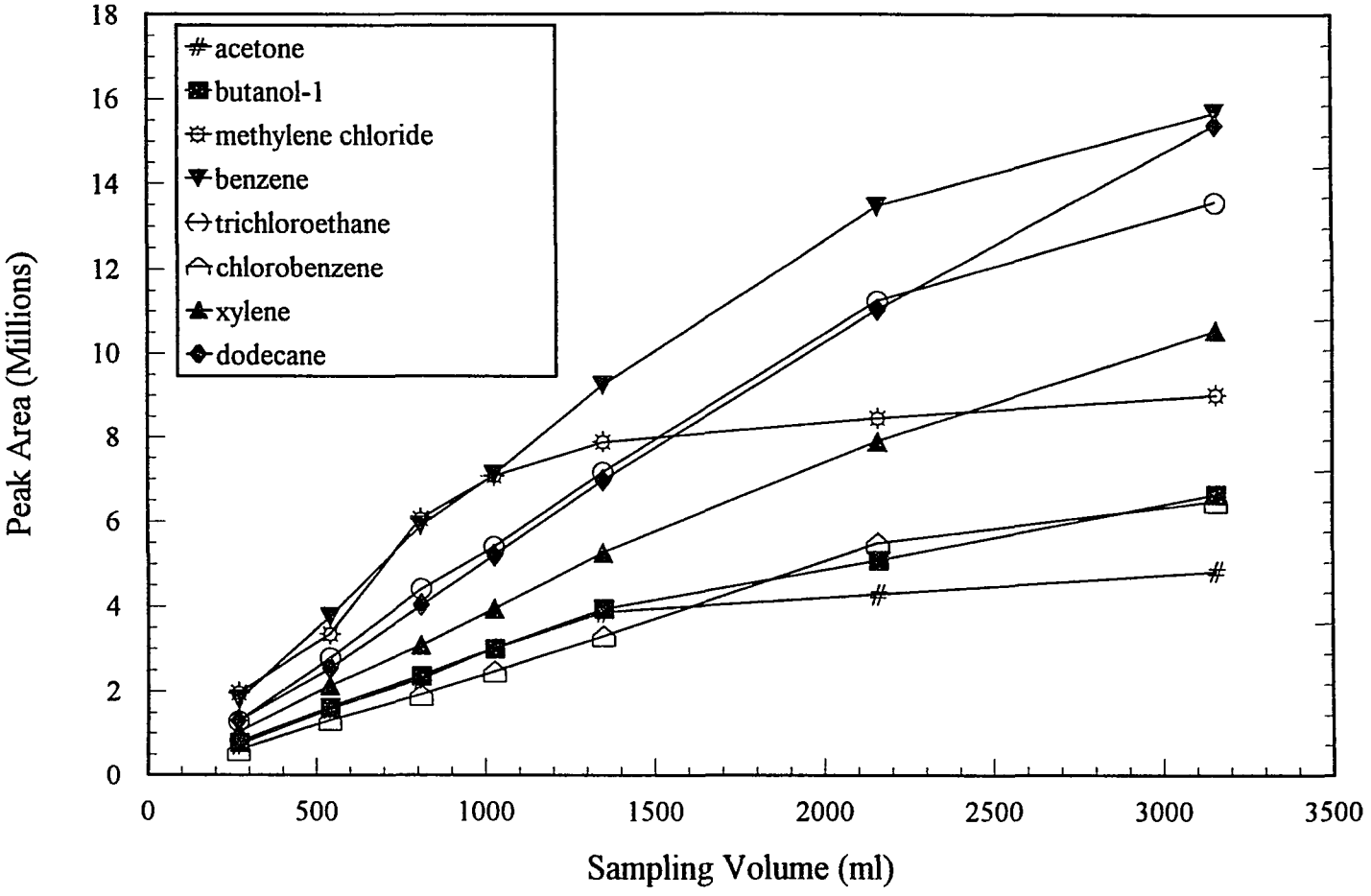


Figure 67 Rsponse of analytical system as a function of sampling volume. The concentration of tested compounds was about 1 ppm and the flow rate was 27 ml/min. The pulse time was 4 seconds and the pulse current was 30 A.

system, no significant effect of moisture was observed. Furthermore, the sampling volume is comparable with that in a cryogenic trap system.

7.3.4 Calibration Curve and Detection Limits

Internal standard calibration can be used in this system. However, it is not easy to select the internal standard since many VOCs might exist in the air sample. In this study, an external calibration has been tested. A series of standard gas mixtures at concentration of 0.05 to 3.5 ppb were prepared in 6 liter canisters. The canister was put in the system described in Figure 61 and the standard gas was pumped through the minitrap for 50 minutes at 20 ml/min. Thus the sampling volume was 1000 milliliters. The calibration curves for some of typical VOCs are presented in Figure 68.

The minimum detection limits can be defined as a response three times higher than the noise. To evaluate the detection limits, a standard gas was diluted with zero grade nitrogen to around 0.1 ppb. This diluted standard gas was analyzed seven times and the standard deviation of concentrations was calculated. The minimum detection limits can be calculated as three times the standard deviation. Table 10 shows the detection limits of some VOCs. For most compounds, the detection limits were from 0.01 to 0.04 ppb.

Table 10 Detection Limits *

Compounds	Hexane	Benzene	Toluene	Ethylbenzene	p-Xylene	Styrene	naphthalene
Detection limits (ppb)	0.020	0.028	0.027	0.021	0.014	0.020	0.022

* Detection Limits was based on three times ratio of signal to noise.

7.3.5 Analysis of Real Ambient Air Sample

Before sampling, canisters should be cleaned by evacuating and filling with zero-grade air four times. The typical chromatogram of system blank is shown in Figure

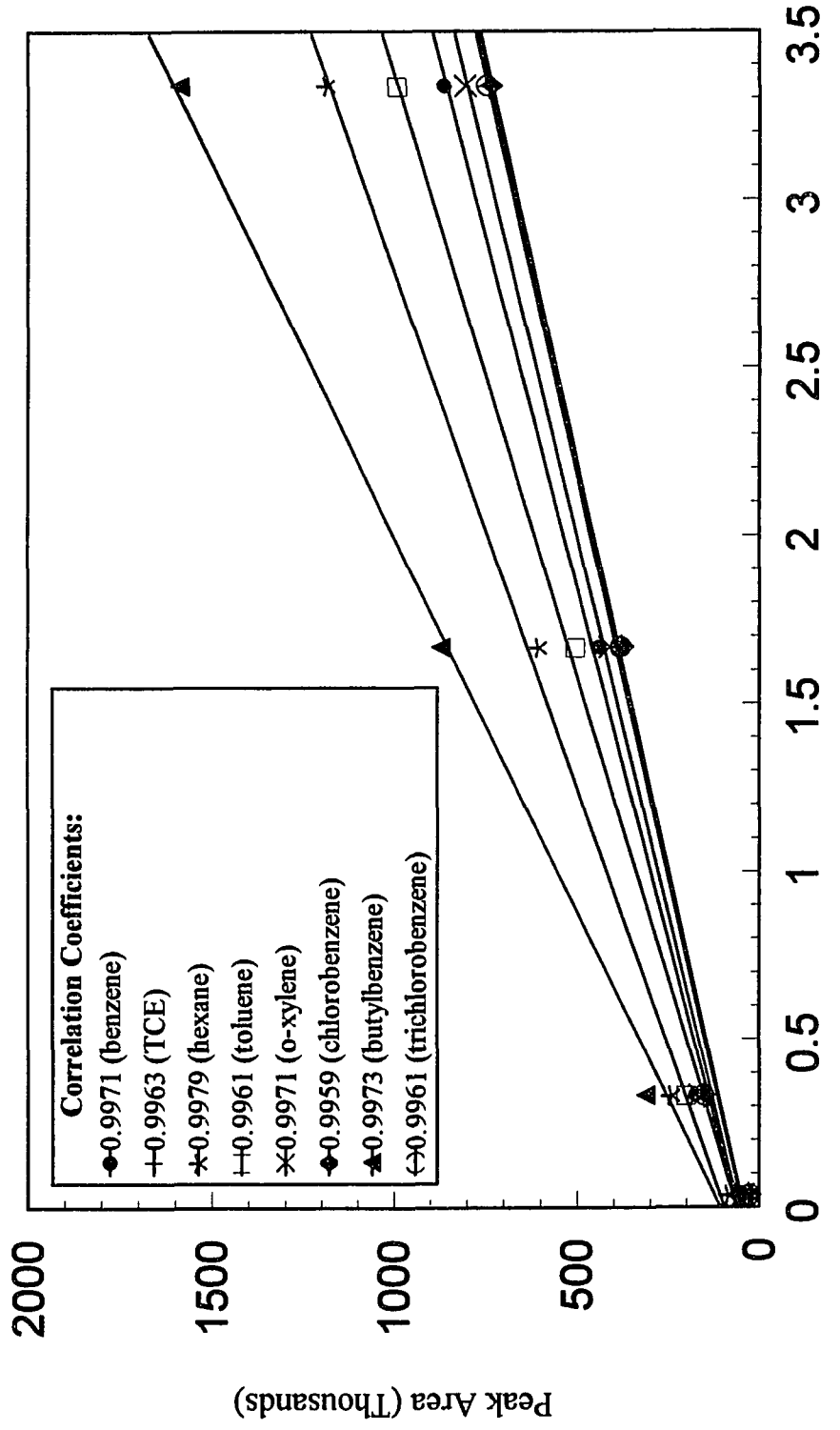


Figure 68 Calibration curve. The sampling volume was 1000 ml. The pulse time was 4 seconds and the pulse current was 30 A.

69a. Figure 69b is a typical chromatogram of standard gas at sub-ppb level. Thus it is easily seen that the analytical system is very clean at this time.

Indoor ambient air at Room 301, Tiernan Hall, NJIT, was sampled using a cleaned Summa™ canister, and the canister was connected to the canister-miontrap system, which is ahown in Figure 61. A 1000 ml air sample was passed through the minitrap using a vacuum pump at a flowrate of 20 ml/min. Then the valve was turned to injection mode and 60 ml dry air purged the minitrap. A heating pulse was applied to desorb analytes from the minitrap. The released analytes were introduced into GC column directly. Figure 70 presents the GC chromatogram of indoor ambient air. A spiked sample was used to identify the toluene peak. It is difficult to use the spike method to identify many of the unknown peak in a real sample. An external standard was used to quantitate the concentration of toluene. The concentration of toluene in this ambient air was 3.29 parts-per-billion.

A 1000 ml of ambient sample was spiked with 20 ml of a standard gas, which contains 2 ppm of toluene, 4.8 ppm of ethyl acrylate and 4.8 ppm of acrylonitrile. The chromatogram of the spiked sample is shown in Figure 71a. Figure 71b shows the chromatogram of another spiked sample, which was spiked 20 ml of 2 ppm of acetone, butanol, methylene chloride, hexane, 1 ppm of benzene, o-xylene and dodecane. An external calibration curve was used to quantitate the concentration of spiked sample. Then the spike recovery was calculated:

$$\text{Spike recovery} = \frac{\text{amount recovered (nl)}}{\text{amount spiked (nl)}} \bullet 100$$

The results of the spike recovery study are shown in Table 11. The spike recoveries were in a range of 85% to 115%.

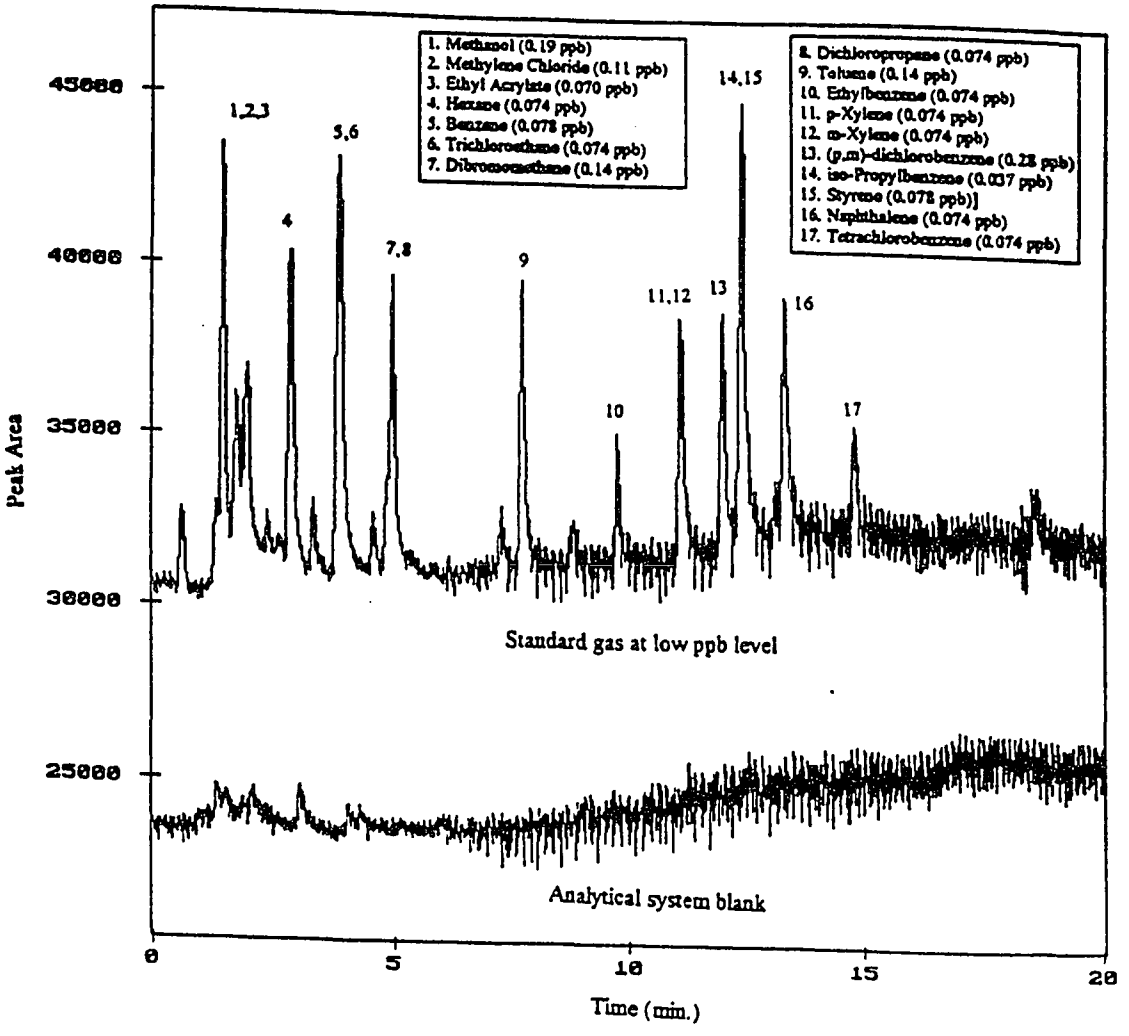


Figure 69 Chromatograms of system blank and standard gas at low ppb level. The sampling volume was 1000 ml. The pulse time was 4 seconds and the pulse current was 30A.

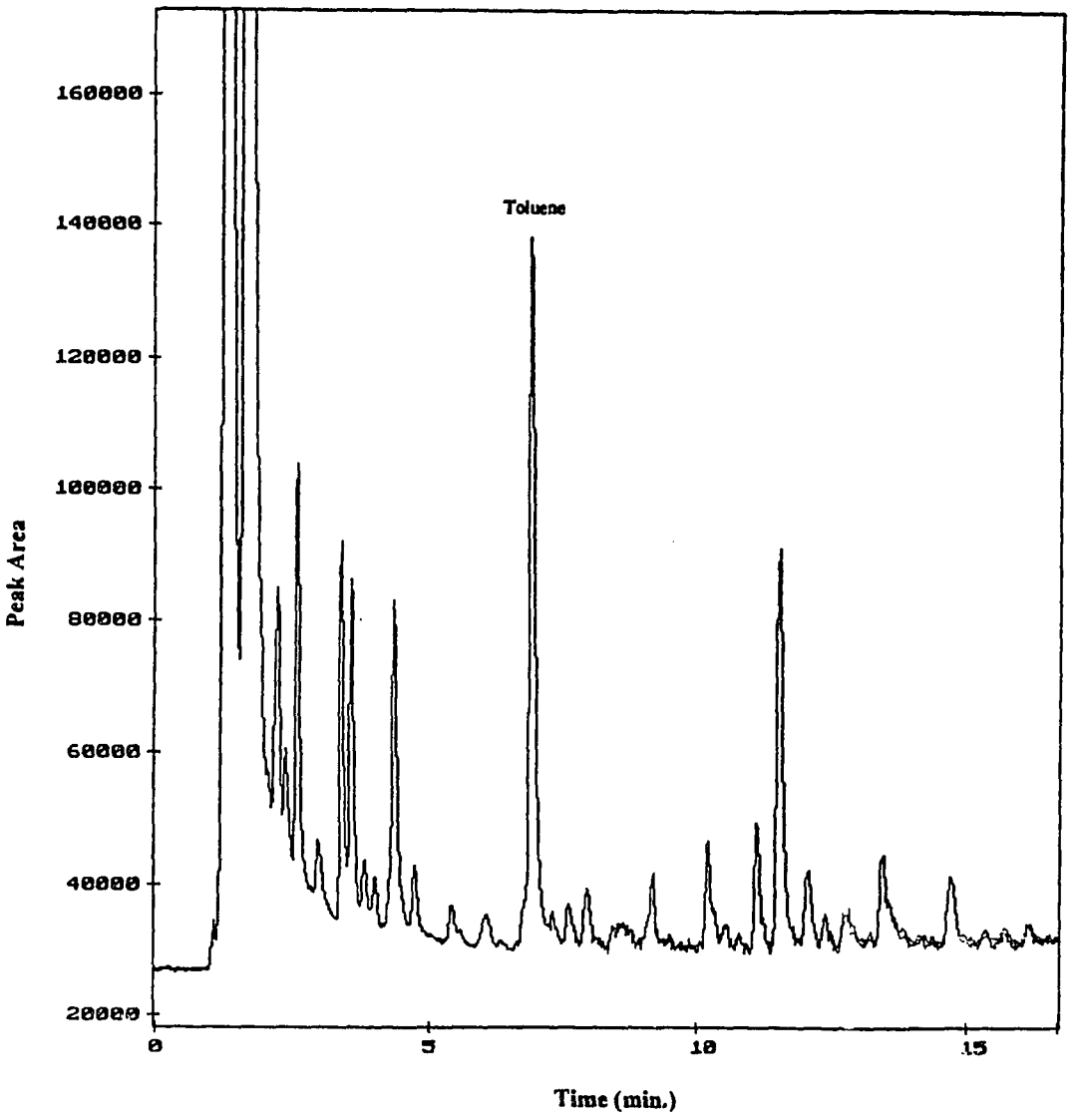


Figure 70 Chromatograms of indoor air using the canister-minitrap system. The sampling volume was 1000 ml.

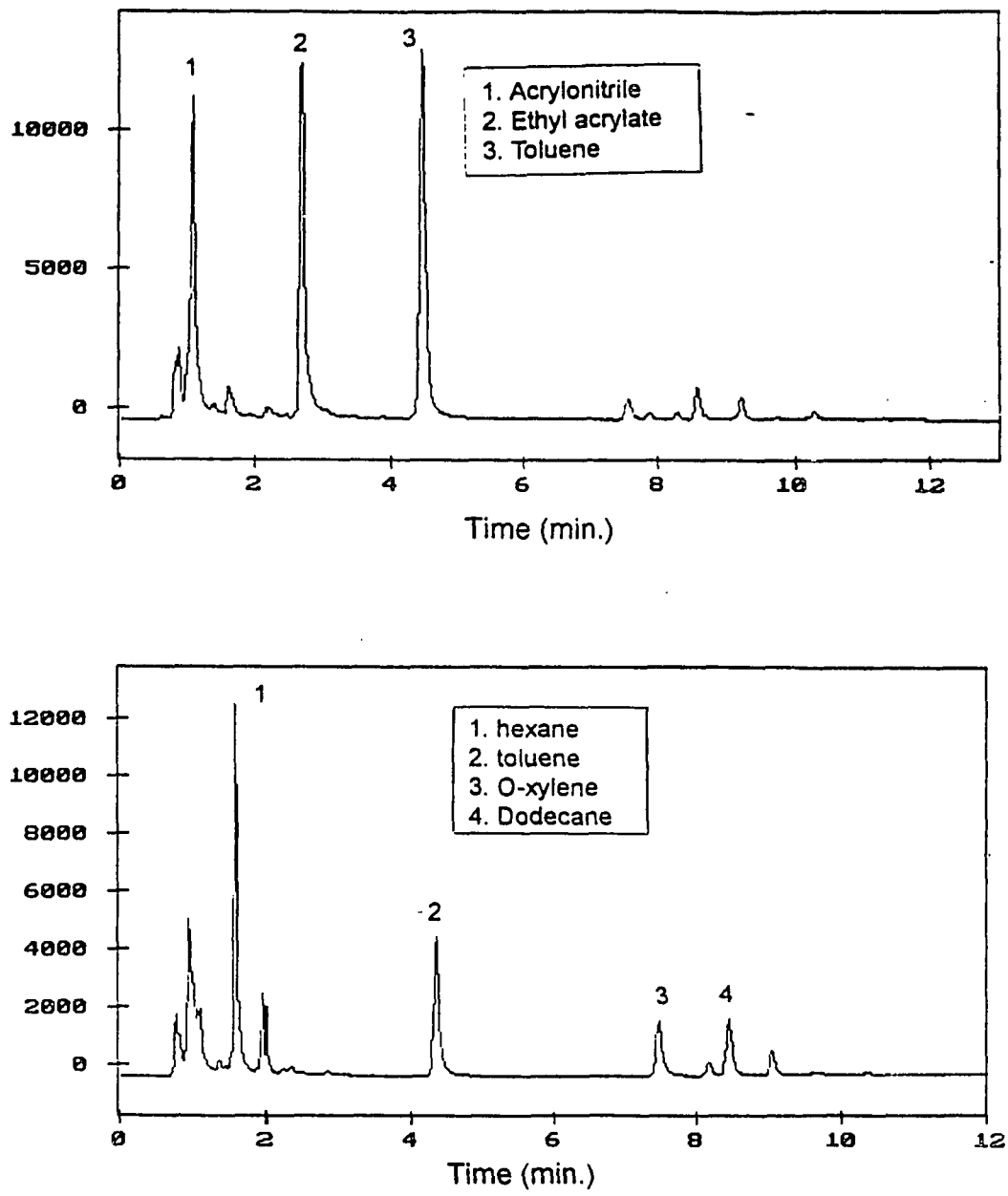


Figure 71 Chromatograms of spiked air samples. 20 ml of standard gas was spiked in 1 liter ambient air.

7.4 Summary

The minitrap can be used as a preconcentration trap to concentrate the VOCs from an air sample taken in a canister and as injection device as well without cryofocus or other refocusing trap. The sampling volume is comparable with cryogenic system and moisture in samples has negligible effect on the performance of the minitrap. The trapping and desorption efficiencies are quantitative for tested compounds (C_2~C_{12}). The detection limits for most VOCs were from 0.01 to 0.05 ppb. The analysis of indoor ambient air has demonstrated that this minitrap-canister system can be used for VOCs analysis of ambient air.

Table 11 Spike Recovery of Some Typical Ozone Precursor

	Amount spiked (nl)	Amount recovered (nl)	Recovery (%)
Ethyl acrylate	96	105	109
Acrylonitrile	96	110	115
Toluene	40	37	93
Hexane	20	20	98
Benzene	20	19	95
O-Xylene	20	17	85
Dodecane	20	18	90

CHAPTER 8

CONCLUSIONS

In this research, microtrap based gas chromatographic systems were investigated for continuous on-line monitoring of VOCs in the gas and water effluents. In the case of air analysis, three injection systems namely gas sampling valve, SVM and OLMT-BF were evaluated and compared in terms of response characteristics and detection limits. It were found that both the SVM and OLMT-BF systems are very sensitive and have low detection limits, and the OLMT-BF system has even lower detection limits than the SVM system. Moreover, the OLMT-BF system can obtain information about the time period between the pulses and track the sample stream at all times. A microtrap based NMOC analyzer was developed for continuous monitoring of NMOC in a gas stream. In these NMOC analyzers, the microtrap was served as a separator for the permanent gases as well as an on-line preconcentrator. The results have demonstrated that these NMOC analyzers has low detection limits and high resistance to permanent gases.

An on-line microtrap and membrane extraction GC system has been developed for continuous monitoring of VOCs at trace levels in water stream. On-line microtrap and membrane extraction device is very effective as an automatic, on-line, sample extractor, preconcentrator as well as injector. The detection limits for most VOCs were at the low ppb level.

The multibed minitrap packed with Carbotrap C, Carbotrap (B) and Carbosieve S-III in series can be used to concentrate VOCs in ambient air and also served as an injector without focusing trap or cryogenic trap. The sampling volume is comparable to cryogenic trap. However, the minitrap-canister system is more convenient and moisture has no significant effect on the performance of the minitrap. The detection limits for hexane, benzene and toluene are 0.02, 0.028 and 0.021 ppb, respectively.

APPENDIX A

MACRO FOR CALCULATION OF EQUATION 3.14

In this appendix, a Matlab macro is presented for the calculation of equation 3.14.

```
clc, i
Ilost=0
for i=1:100
x=[0:0.1:i/17.5];
y=exp(-x.^2)/2);
Function y = humps (x)
plot(x,y);
k=1/√2π ;
t=i/(100/√N )
q=quad('humps',0,x)
lost=0.5-k*q
Ilost=lost+Ilost
end
Ilost
```

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