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SAMPLING AND ANALYSIS OF TRACE LEVEL VOLATILE ORGANIC COMPOUNDS FROM AIR VIA MEMBRANE PERMEATION

by
Naihong Zhu

A Dissertation
Submitted to the Faculty of
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APPROVAL PAGE

SAMPLING AND ANALYSIS OF TRACE LEVEL VOLATILE ORGANIC COMPOUNDS FROM AIR VIA MEMBRANE PERMEATION

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ABSTRACT

SAMPLING AND ANALYSIS OF TRACE LEVEL VOLATILE ORGANIC COMPOUNDS FROM AIR VIA MEMBRANE PERMEATION

by
Naihong Zhu

The objective of this study is to develop air sampling techniques using membrane permeation. Two novel techniques for sampling and analysis of trace level VOCs from air via membrane permeation are presented:

(1) selective concentration of VOCs into a canister using a membrane permeator;

(2) on-line membrane extraction for direct introduction of VOCs from air emissions into a gas chromatograph.

In the membrane permeator-canister sampling system (MPCS), the air sample containing trace level VOCs as well as some interferences such as moisture are passed through the membrane module. Polydimethyl siloxane membrane used in this research is highly permeable to organic compounds, but relatively impermeable to air and water. The membrane permeator used in the experiments acts as a barrier that allows selective diffusion of the organics and elimination of water. Parameters that control the membrane permeation, such as the effect of membrane thickness, the effect of membrane module configuration, as well as the effect of operating parameters, i.e., temperature, sample flow rate, pressure difference, sampling time etc., were investigated. The MPCS system was evaluated by collecting real ambient air samples. The study demonstrated that membrane

sampling can offer several advantages, such as, elimination of water vapor from the background matrix and sample preconcentration thus enhancing the sensitivity.

In the second project, an on-line membrane extraction microtrap GC (OLMEM-GC) monitoring system was developed for selectively extracting and monitoring trace volatile organic compounds from an emission stream. A laboratory scale catalytic incinerator was used to generate emission streams containing VOCs. The conversion efficiency of the incinerator was evaluated using the OLMEM-GC system. Continuous monitoring of VOCs was achieved by first selectively permeating VOCs through the semipermeable membrane and then using a microtrap to concentrate and inject the permeated VOCs into the GC. The method detection limit, precision, system linearity, response time, as well as the effects of operating parameters such as pressure difference, sample flow rate, temperature, and moisture content were investigated.

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Zhu, N., S. Mitra, and Z. Li, "Application of On-line Membrane Extraction Microtrap Gas Chromatography (OLMEM-GC) for Continuous Monitoring of VOCs Emission," *J. of Microcolumn Separations*, (in press), 1996.

Zhu, N., X. Zhang, and S. Mitra, "On-line Membrane Extraction Microtrap GC System for Monitoring VOCs," *The 18th International Conference on Capillary Chromatography*, Riva del Garda, Italy, May 1996.

Mitra, S., N. Zhu, X. Zhang, and B. Kebbekus, "Continuous Monitoring of Volatile Organic Compounds in Air Emission Using On-line Membrane Extraction Microtrap GC System," *J. of Chromatogr.*, A, vol. 736, pp. 165-173, 1996.

Mitra, S., L. Zhang, N. Zhu, and X. Guo, "Characteristics of On-line Membrane Extraction Microtrap GC System as Applied to Air and Water Monitoring," *J. of Microcolumn Separations*, vol. 8(1), pp. 21-27, 1996.

Dauerman, L., G. Windgasse, N. Zhu, and Y. He, "Microwave Treatment of Hazardous Wastes: Physical Chemical Mechanisms," *Microwave Processing of Materials III*, MRS symposium proceedings, Vol. 269, pp. 465-470, 1992.

Zhu, N., L. Dauerman, H. Gu, and G. Winddgasse, "Microwave Treatment of hazardous Wastes: Remediation of Soils Contaminated by Non-Volatile Organic Chemicals Like Dioxins," *J. of Microwave Power and Electromagnetic Energy*, Vol. 27, No. 1, 1992.

Zhu, N., "Microwave Treatment of Hazardous Wastes: 'Chemical Fixation' of Insoluble, Non-Volatile, Chemical Non-Reactive Organics in Soils," *Mini-Technical Conference*, Society for the Advancement of Material and Process Engineering, April, 1991.

Xiao, H., and N. Zhu, "The Varying Law of Acidic Properties of Phenols and Their Nitroderivatives," *J. of the East China Institute of Technology*, 1984.

This dissertation is dedicated to
Harry and Kelly

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NOMENCLATURE

A	area of the membrane surface
C	concentration
C_i	concentration of the component i; or the concentration at the inner wall of the hollow fiber
C_{hb}	concentration of the component i in the feed side (or high pressure side)of bulk phase
$C_{if(m)}$	concentration of the component i in the membrane of the feed interface
$C_{ip(m)}$	concentration of the component i in the membrane of the permeate interface
C_o	concentration at the outer wall of the hollow fiber
C_{lb}	concentration of the component in the vacuum or low pressure side of the membrane module
d_i	inner diameter of the hollow fiber
d_o	outer diameter of the hollow fiber
D_i	diffusion coefficient of the component i
E_d	activation energy
ΔH_s	Heat needed to dissolve the permeant in the membrane
J_i	permeation flux of the component i
K_f	distribution coefficient between the membrane and the feed side gas phase
K_p	distribution coefficient between the membrane and the vacuum side gas phase
l	length of fiber
L_i	proportion coefficient
L_t	the lag time
N	the number of the fibers in a membrane module
N_{Re}	Reynolds number

N_{Sc}	Schmidt number
P_i	permeability of the component i
p_{ip}	partial pressure of analyte in the permeate side of membrane
p_{if}	partial pressure of analyte in the feed side of membrane
p''	total pressure in the permeate side
p'	total pressure in the feed side
r_i	inner radii of the hollow fiber
r_o	outer radii of the hollow fiber
r_{lm}	logarithmic mean radii of the hollow fiber
R	overall mass transfer coefficient in the membrane module defined by equation 5.7
R_g	mass transfer coefficient in feed side gas phase
R_m	mass transfer coefficient for mass transfer across the membrane
Rv	mass transfer coefficient in the vacuum side gas phase
S_i	solubility coefficient of the component i
V_i	the molar volume of the component i

GREEK SYMBOLS

α	selectivity of a membrane
δ	the film thickness
γ_i	the activity coefficient of the component i
Φ	pressure ratio across a membrane
μ	viscosity
μ_i	the chemical potential of the component i
μ_{if}	the chemical potential of the component in the feed side of the membrane
$\mu_{if(m)}$	the chemical potential in the membrane at the feed interface
μ_{ip}	the chemical potential of the component in the permeate side of the membrane
$\mu_{ip(m)}$	the chemical potential in the membrane permeate interface
ν	sample linear velocity
ρ	density

CHAPTER 1

GENERAL INTRODUCTION

Volatile organic compounds (VOCs) have received much scrutiny from the regulatory community because many of these compounds are toxic/mutagenic and also participate in the photochemical reactions that lead to smog formation. VOCs encompass a wide range of compounds, and are defined by US EPA as organic compounds with a vapor pressure greater than 0.01 kPA at 25°C. While many of the VOCs may not be highly toxic at the levels commonly encountered in ambient air, they lead to ozone formation in the troposphere, which poses serious public health problems.

Existing regulations pertaining to air quality were significantly expanded in the Clean Air Act Amendments (CAAA) of 1990. Titles I, III and V of this act have direct relevance to VOCs emissions. Title I deals with priority pollutants, ozone being one of them. Controlling VOCs is known to be one of the most effective ways of controlling urban ozone. Under this provision, State Implementation Plans must keep current inventories of emissions from all major sources. One hundred and eighty-nine compounds are listed in Title III of the CAAA as hazardous air pollutants or HAPs. Many of the VOCs are in this list and are defined as HAPs. According to this regulation any major source emitting 10 tons per year of any single HAP or, 25 tons per year of total HAPs must reduce emission using state of the art Maximum Achievable Control Technology (MACT). The Title V of this act deals with permitting requirements for these VOCs. Besides the CAAA, industries are required by the Community Right to Know Act included in the Superfund Amendments and Reauthorization Act to report accidental and routine releases of listed chemicals.

It is clear that the development of a rapid and efficient analytical method for identification and quantitation of trace level of VOCs is of utmost importance for compliance of the regulations briefly mentioned above. These regulations are also requiring manufacturing facilities to implement a variety of VOCs control devices such as carbon adsorption, condenser systems, wet scrubbing, biodegradation, membrane separation, and incineration. Thus, in addition to the routine air analyzing methods, sensitive, continuous monitoring methods are also needed to provide real-time (or near-real time) detection and quantitation of emissions from these control devices so that proper functioning of the devices can be ensured.

Traditional methods of analysis of VOCs in ambient air and stack emissions use either whole air samplers such as Tedlar bags and canisters (e.g., EPA Method TO-14), or sorbent cartridges (e.g., EPA Method TO-1 & 2). Among those routine air analytical methods, canister analysis method (EPA TO-14) is the most popular one. The canister is a sampling device used to collect and store whole air samples. It can be pressurized, thereby increasing the air volume collected. However, in the canister analysis, too much moisture will cause severe interference. It limits the sample quantity from which VOCs can be preconcentrated as it freezes in the cryogenic trap. Moisture may clog the cryogenic trap and the capillary interface. The other limitation of canister sampling is that it samples the "whole air" and provides no selectivity towards the VOCs.

EPA methods mentioned above are very useful for routine analysis of air sample. However, in those methods, the air samples are collected in the field and the analysis is done in the laboratory. Consequently, there is a significant delay between sampling and analysis. Moreover, there may be inaccuracies associated with sampling, sample transportation and storage. Also most of these techniques require extensive sample handing that increases the analysis cost per sample. At present, there is a real need for instrumentation that can be used to carryout automated, on-line analysis to provide real-time (or near-real time) information, to be used for process control and for meeting regulatory compliance. Techniques such as mass sepctrometry and FTIR are being used as on-line monitoring techniques. However, in environmental application, interference from moisture and band overlap are serious problems faced by these techniques. Since a typical environmental sample may contain dozens of compounds, without chromatographic separation, the identification and quantitation of trace level VOCs in a complex sample is quite difficult, if not impossible.

In recent years membranes have been used in analytical techniques to extract organic compounds from both air and water [e.g., Kotiaho et al. (1991); Mitra et al (1994, 1995); Yang et al. (1994); Melcher and Morabito, (1990)]. Along with the first analytical application of a membrane described by Hoch and Kok [Hoch and Kok, (1963)], a significant amount research has been devoted to interfacing waster samples directly to a mass spectrometer [e.g., Bauer and Solyom, (1994); Lapack and You, (1991); Silivon et al. (1991)]. Despite the three decades of development in analytical membrane technology, little information is available on its use in air sample and sample preparation for chromatography. Moreover, there is a great deal of data in the literature concerning permeation of gases through polymer membranes and much less data on the permeation of organic compounds. Therefore, the factors that affect VOC permeation are less well understood.

The general purpose of this research was to explore the possibilities of using membrane technique for sampling and analyzing trace level VOCs from air. For the past few years we have been working on the development of membrane based sampling system. Efforts have been made for developing a membrane permeator for canister as well as for on-line membrane extraction. Both systems: Membrane-Canister Sampling System and On-line Membrane Extraction Microtrap GC System (OLMEM) have been designed and their performance have been tested and evaluated by collecting and analyzing the real samples. The study has demonstrated that the membrane extraction technique can be utilized to selectively enhance the concentration of VOCs from a complex air matrix into a canister or a on-line monitoring device with no any sample preparation, which increases the sensitivity of VOCs analysis and lows the detection limit.

In general, membrane permeation is a complex process that involves chemical interactions, mass transfer, partitioning onto the membrane, and diffusion of the analyte through the membrane. Thus a permeation process is sensitive to operating variables such as partial pressure gradient, temperature, flow condition, moisture in the sample, etc. The optimization for all those operating parameters has been investigated. In addition, some characteristics of membrane extraction of VOCs such as the relationship between membrane structure (membrane material and thickness), permeation rate, and the enrichment of VOC; response time for a membrane permeation process; the time dependent permeation rate; etc. also have been studied, which provide useful information on the mechanism of permeation of VOCs existed in parts per million or parts per billion levels in air matrix.

The structure of this paper was organized as follows: the review of the literature concerning the membrane extraction of VOCs is presented in Chapter 2; the objective and the scope of the study, in Chapter 3; the Membrane Permeator Canister Sampling System (MPCS) design, operation, and the optimization, in Chapter 4; evaluation of different membranes in MPCS and analysis of real-world samples in Chapter 5; Developments in OLMEM-GC in Chapter 6. Application of OLMEM-GC in monitoring effluents from a catalytic incinerator is Chapter 7. While the results of the experimental work are discussed in each chapter in which such results are presented, the overall conclusions are presented in Chapter 8. The list of symbols (nomenclature and Greek symbols) is listed at the beginning and the list of references is given at the end of the paper.

CHAPTER 2

LITERATURE REVIEW

There are a number of different topics which are pertinent to the work performed during the course of this dissertation. They involve the routing and on-line analytical methods of volatile organic compounds as well as pertinenting regulations; membrane separation technologies; microtrap adsorption and desorption; different approaches to air monitoring. Membrane permeation is key to this project and will be reviewed in detail in this chapter. Some of the other topics are reviewed and discussed in the individual project descriptions.

2.1 Definition of Membrane

Many attempts have been made to give a general and correct definition of membrane. However, as it has been mentioned by Paul and Yampol'skii in a witty manner: any absolute definition of a membrane will be, most likely, incorrect; any correct definition will be incomplete [Paul and Yampol'skii, (1994); Dukhin, et al. (1991)]. Ho and Sirkar defined a membrane as follows [Ho and Sirkar, (1992)]:

> The membrane is an interphase between two bulk phases.
>
> The membrane phase may be any one or a combination of the following: nonporous solid, microprorous or macroporous solid with a fluid (liquid or gas) in the pores, a liquid phase with or without a second phase, or gel.

According to Paul, Meares, Hwang, Nikolaev and other investigators, the most general definition may be the following [Paul and Yampol'skii, (1994); Meares, (1961); Hwang and Kammermeyer, (1975); Nikolaev, (1980)]:

> A membrane is a phase or a group of phases that lies between two different phases, which is physically and/or chemically distinctive from both of them and which, due to its properties and the force field applied, is able to control the mass transport between theses phases.

A membrane process allows selective and controlled transfer of one species from one bulk phase to another bulk phase, separated by the membrane.

2.2 Historical Background of Membrane Permeation of VOCs

2.2.1 Membrane Separation

The phenomenon of gases separation with membrane has been known for more than 150 years, but significant commercial practice did not emerge until the late 1970s [Paul, (1994)]. A summary of the development of this technology is provide in Figure 2.1 based on publications by Paul. Systematic studies related to membrane gas separation can be traced to the nineteen century. J. K. Mitchell might be the first one to make scientific observations of gas separation by membrane in 1831. He observed that hydrogen filled a balloon made of natural rubber faster than air [Kesting, (1985); Paul, (1994)]. At almost same time, A. Fick, a physiologist, studied gas transport across membranes which led to the formulation of what is known today as the Fick's first law. However, the work which determined the direction of the research for many decades was published by Thomas Graham in 1866 [Baker and Wijmans, (1994); Kesting, (1985); Koros, (1990)]. Graham

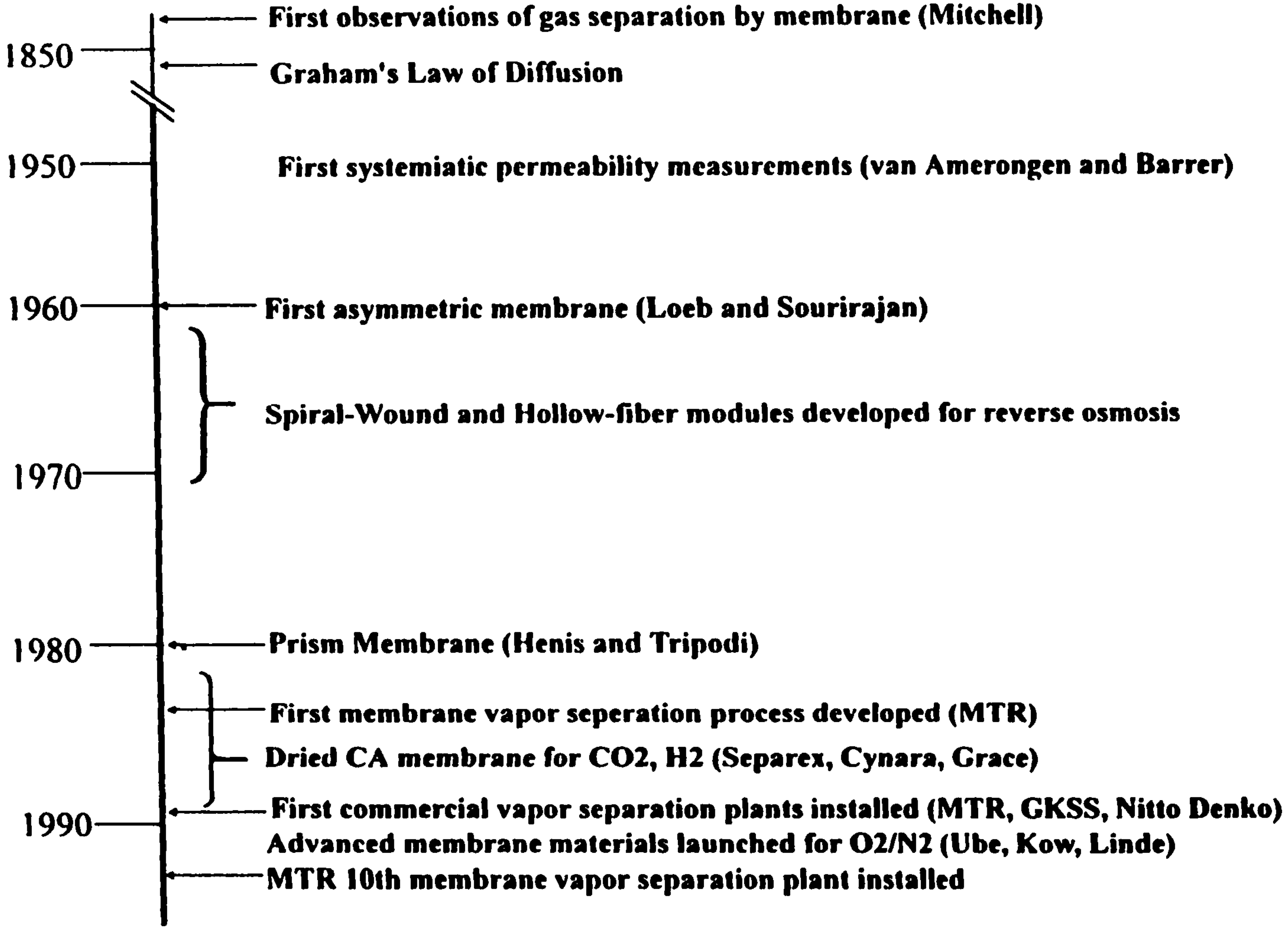


Figure 2.1 Development of gas and vapor membrane separation technoloy.

repeated Mitchell's experiments with natural rubber and obtained the first quantitative measurements of the rate of gas permeation. He carried out the first membrane gas separation and obtained oxygen enriched air containing 46.6% oxygen. His studies on porous membranes led to Graham's law of diffusion. At that time, some development of physical and chemical theories, such as Maxwell's kinetic theory of gases used the concept of a perfectly permselective membrane as a theoretical tool. In the early 1940s and 1950s, van Amerongen, Barrer, Stern, Meares, and others laid the foundation of modern theories of gas separation with membrane.[Amerongen, (1950); Barrer, (1941); Stern, (1972); Meares, (1965), Baker and Wijmans, (1994)]. The solution-diffusion model, which is used to today, developed at this time.

Despite the availability of interesting polymer materials, membrane fabrication technology was not advanced enough to make useful membranes from these polymers. Therefore, the widespread use of gas separation membranes has occurred only within the last 15 to 20 years. The Loeb-Sourirajan membrane was the first work which transformed membrane separation from the laboratory research to an industrial process and made reverse osmosis a practical technology (early 1960s) [Loeb and Sourirajan, (1963); Toshima, (1992)]. The first large-scale gas separation modules were developed by DuPont as early as 1970s, but the first successful commercial gas separation by membrane permeation process were announced by Monsanto in the late 1970s which launched its hydrogen-separating Prism® membrane in 1980 [Ho and Sirkar, (1992); Baker, (1994)]. Monsanto's technical and economic success spurred other companies, such as Separex and Grace, to develop their own membrane techniques. Since then, there is a great deal of data in the literature concerning permeation of gases through polymer membrane, but much less data on the permeation of organic vapors. Therefore, the factors that affect vapor permeation are less well understood.

In 1982, the first membrane vapor separation process was developed by Membrane Technology and Research, Inc.(MTR) using rubbery composite membrane to recover organic vapors from air [Baker, et al. (1984); Peinemann, Mohr, and Baker, (1986); Baker, Yoshioka, Mohr, and Khan, (1987); Baker, (1985)]. This technology was based on the selective solubility in the membrane material. During a solvent recovery process, the contaminated air stream from an industrial source flows past the surface of a membrane which is much more permeable to organic vapors than to air. The solvent vapor on the permeate side of membrane is then compressed, cooled, and condensed. Their investigations had shown that membranes used to recover low concentration of organic solvents from air had extremely high membrane selectivities and were from 10 to 10,000 times (typically 20 to 100) more permeable to organic solvents than air (Figure 2.2). For the several years, MTR was the only company practicing in this field. In later 1980s and early 1990s, GKSS (German) and Nitto Denko (Japan) became involved in this technology and set up more than 10 vapor-separation plants [Bechling, et. al. (1989); Ohlrogge, et al. (1990); Matsumoto, et al. (1991); Koros and Chen (1987)].

2.2.2 Membrane Technology Used in Analytical Applications

Analytical applications using membranes also can be dated back to the early 1960s. In 1963, membrane introduction mass spectrometry was first introduced by Hoch and Kok to study the reaction kinetics photosynthesis [Hoch and Kok, (1963)]. Another early application membranes in MS was the use of a polymer as an interface in GC/MS, which

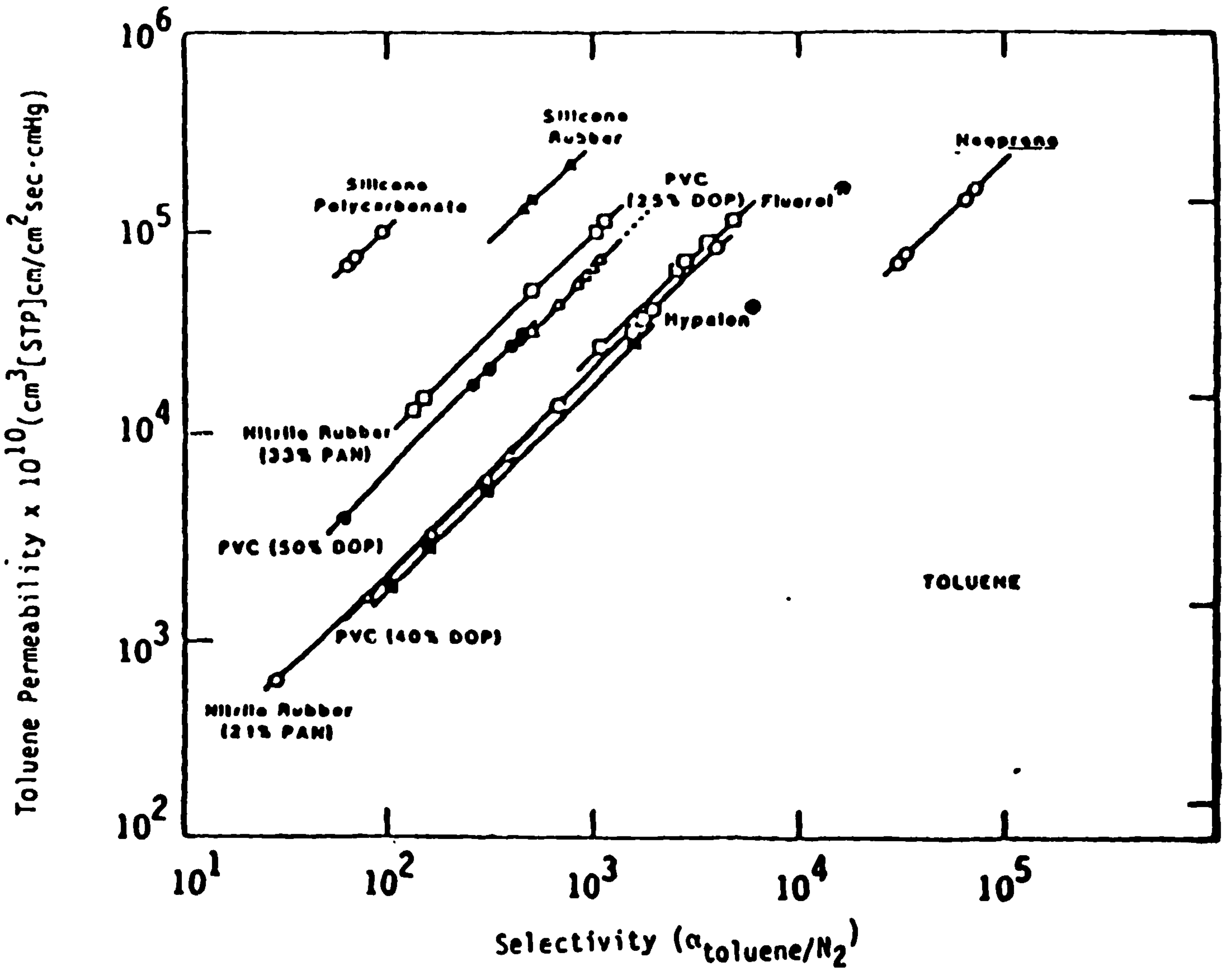


Figure 2.2 Permeability vs selectivity for toluene in various rubber membrane at 40 0C [Baker].

depends on the low permeability of helium relative to organic compounds. In 1969, membrane introduced MS was first used to monitoring a fermentation process which is commonly used today [Llewellyn, and Littlejohn, (1969); Reuss, et al. (1975)].

Along with the first analytical applications of a membrane described by Hoch and Kok, a significant amount of research has been devoted to interfacing air and water samples directly to a mass spectrometer. Kotiaho et al. provided a review on the theories and applications of this combined technique [Kotiaho, et al. (1991)].

Although many early methods used a flat, supported membrane, it has been found that a hollow fiber has a more useful geometry for analytical applications. Since the first hollow silicone fiber application introduced by Westover and co-workers, most of the recent developments in membrane techniques have focused on the use of hollow-fiber geometry [Westover, Tou, and Mark, (1974)]. For example, Brian J. Harland and co-workers carried out a series of studies to determine VOCs in aqueous samples by membrane inlet MS and extended the analysis to the field for continuous monitoring of the levels of Benzene, Toluene, and Xylene in an industrial effluent stream [Harland, et al. (1987)]. Lapack research group set up a Membrane MS for the direct trace analysis of VOCs in air and water [Lapack, Tou, and Enke, (1990)]. S. J. Bauer and R. G. Cooks conducted a study to determine organic analytes in an on-line process using a membrane MS [Bauer and Cooks, (1993)]. Recently, Pawllszyn co-workers has carried out a series of investigations on water monitoring system based on the membrane extraction and GC cryotrapping [Pawllszyn, et al. (1992, 1994)]. Moreover, Melcher and co-workers described the use of hollow fibers and organic solvent as the stripping phase for introducing analyte into a liquid chromatograph [Melcher, et al. (1992)]. Also, a combined technique of hollow fiber separation with high density carbon dioxide extraction has be reported for the analysis of semivolatile organic compounds in water [Yang and Pawliszyn, (1993)].

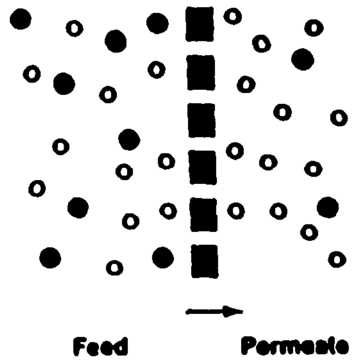
2.3 The Basic Principles of Membrane Permeation

The principal property of membrane used in separation and analytical applications is the ability to control the permeation of different species. Two models are used to describe the permeation process: the poreflow model and the solution-diffusion model. Based on those models, membranes usually can be classified as porous or non-porous as summarized in Figure 2.3.

2.3.1 Porous Membrane and the Poreflow Model

Depending on solute size, porous membranes are either microporous or macroporous. By IUPAC classification, pores of less than 20 $\overset{0}{A}$ in diameter are micropores. Pores between 20 and 500 $\overset{0}{A}$ are called macropores. If membranes contain pores which are large enough to allow convective flow, separation will not occur. However, if the size of the pores is smaller than the molecules' mean free path, then Knudsen diffusion replaces convective flow, in which permeating molecules interact with the pore walls much more frequently than with one another. Small molecules are able to diffuse more rapidly than heavier molecular weight species, and separation occurs. The poreflow model is used to explain this permeation process, in which, species are separated by pressure-driven flow through tiny pores. A separation is achieved between different species because one is excluded

Porous membrane



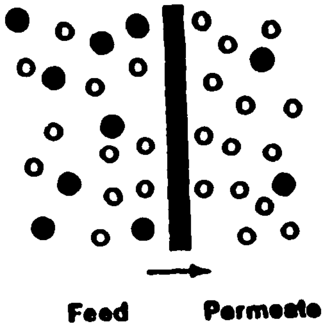
The poreflow model

1. Separation: pressure-driven flow through pores

2. One of the substances is excluded; other permeant is passed

Separation factor $n = \sqrt{\frac{M_b}{M_a}}$

Non-porous membrane



The solution-diffusion model

1. The permeant "dissolves" in the membrane

2. diffuses through the membrane towards the side of the lower concentration

3. desorbed on the side of the lower concentration.

Separation factor $= \frac{\text{Perm gas A}}{\text{Perm gas B}}$

Figure 2.3 Polymeric membrane

(filtered) from some of the pores in the membrane through which other move [Ho and Sirkar, (1992); Wijmans and Baker, (1995)]. This type of diffusion process does not provide sufficient separation in most cases. The molecular sieving is potentially useful in separating molecules of different sizes. However, current membrane materials are too fragile, and it is difficult to fabricate those membranes with the narrow pore-size distribution required by molecular sieving. Besides, water and other vapors usually will condense within the fine pores and block them, seriously affecting the transport rates across the membranes. Therefore, porous membranes are not used commonly in membrane analytical applications.

2.3.2 Non-Porous Membrane and the Solution-Diffusion Model

The membranes currently used in most commercial applications are non-porous membranes. Virtually all of today's non-porous membrane are made of polymeric materials. Mass transport through non-porous (also called homogeneous) membrane, in contrast to mass transport through filter paper or other porous material (Knudsen flow or Poiseuille flow), occurs by activated diffusion and is generally analyzed using the solution-diffusion model.

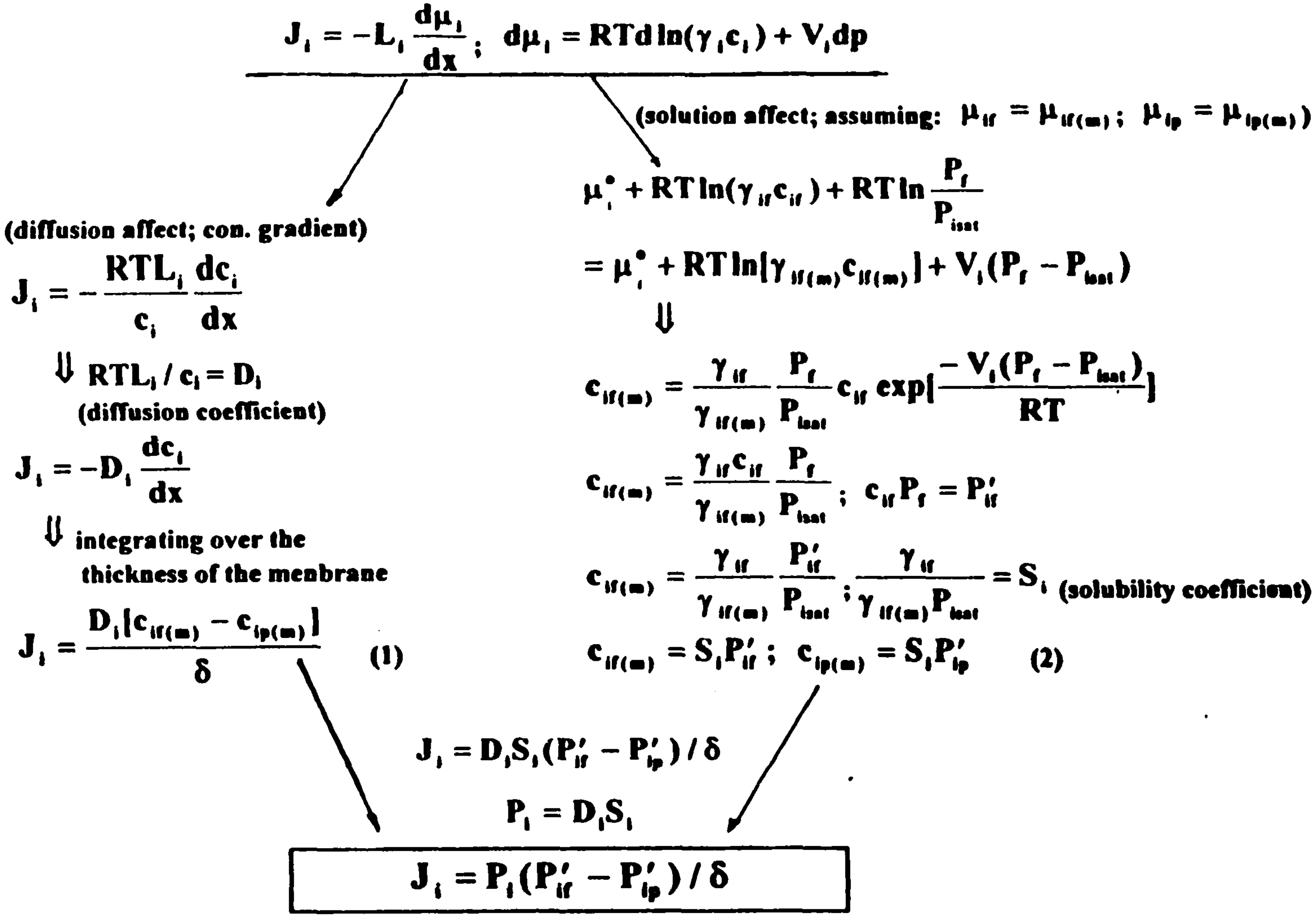
The solution-diffusion model was first proposed by Thomas Graham in 1886 and first shown to be consistent with experimental results by Van Amerogen [Paul, (1994); Amerogen, (1946, 1950, 1964)]. This model postulates that a permeation occurs through the following steps: First, permeant at the high-pressure (or high-concentration) side of the membrane dissolves in the membrane material. Then it diffuses down a concentration gradient to the low-pressure side of the membrane, a process which depends on the formation of "hole" in the plastic network due to thermal agitation of the polymer chain segments. Finally, the permeant becomes desorbed on the side of the lower pressure. A separation is achieved between different species due to the differences in the amount of molecules in the membrane and the rate at which the molecules diffuse through the membrane[Baker and Wijmans, (1994); Prasad, et al. (1994); Alexander, (1966, 1994); Wijmans and Baker, (1995)].

A detailed summary of the solution-diffusion model is provided in Figure 2.4. The model assumes that the gas phases on either side of the membrane are in thermodynamic equilibrium with the membrane material at the interface, which means that there is a continuous gradient in chemical potential from one side to the other side of the membrane. It is also assumed that the interfacial sorption and desorption processes are rapid compared to the rate of diffusion through the membrane. The movement of any species across the membrane is caused by one or more driving forces, such as gradients in concentration, pressure, temperature, electromotive force, etc. All these common driving force can be reduced to chemical potential gradients. Thus, the permeation flux, J_i, of a component, i, can be described by the following simple equation:

$$J_i = -L_i \frac{d\mu_i}{dx} \tag{2.1}$$

If the driving forces are restricted only to concentration and pressure gradients, the chemical potential then can be written as follows:

$$d\mu_i = RTd\ln(\gamma_i C_i) + V_i dp \tag{2.2}$$



$$J_i = -L_i \frac{d\mu_i}{dx};\quad d\mu_i = RT\,d\ln(\gamma_i c_i) + V_i\,dp$$

(diffusion affect; con. gradient)

$$J_i = -\frac{RTL_i}{c_i}\frac{dc_i}{dx}$$

⇓ $RTL_i / c_i = D_i$

(diffusion coefficient)

$$J_i = -D_i\frac{dc_i}{dx}$$

⇓ integrating over the thickness of the menbrane

$$J_i = \frac{D_i[c_{if(m)} - c_{ip(m)}]}{\delta} \qquad (1)$$

(solution affect; assuming: $\mu_{if} = \mu_{if(m)}$; $\mu_{ip} = \mu_{ip(m)}$)

$$\mu_i^{\circ} + RT\ln(\gamma_{if}c_{if}) + RT\ln\frac{P_f}{P_{isat}}$$

$$= \mu_i^{\circ} + RT\ln[\gamma_{if(m)}c_{if(m)}] + V_i(P_f - P_{isat})$$

⇓

$$c_{if(m)} = \frac{\gamma_{if}}{\gamma_{if(m)}}\frac{P_f}{P_{isat}}c_{if}\exp\left[\frac{-V_i(P_f - P_{isat})}{RT}\right]$$

$$c_{if(m)} = \frac{\gamma_{if}c_{if}}{\gamma_{if(m)}}\frac{P_f}{P_{isat}};\quad c_{if}P_f = P'_{if}$$

$$c_{if(m)} = \frac{\gamma_{if}}{\gamma_{if(m)}}\frac{P'_{if}}{P_{isat}};\quad \frac{\gamma_{if}}{\gamma_{if(m)}P_{isat}} = S_i \text{ (solubility coefficient)}$$

$$c_{if(m)} = S_iP'_{if};\quad c_{ip(m)} = S_iP'_{ip} \qquad (2)$$

$$J_i = D_iS_i(P'_{if} - P'_{ip})/\delta$$

$$P_i = D_iS_i$$

$$\boxed{J_i = P_i(P'_{if} - P'_{ip})/\delta}$$

Figure 2.4 The solution-diffusion model

Considering the diffusion effect and integrating over the thickness, δ, of the membrane, Equation 2.1 and 2.2 can be combined to obtained a equation which has the same form as Fick's law:

$$J_i = \frac{D_i\left[C_{if(m)} - C_{ip(m)}\right]}{\delta} \tag{2.3}$$

However, for non-porous membrane permeation, the solution effect also has to be considered. The general approach is to use the assumption mentioned before:

$$\mu_{if} = \mu_{if(m)}; \quad \mu_{ip} = \mu_{ip(m)} \tag{2.4}$$

Then, the concentrations of component i in the feed and permeated side of membrane can be obtained by the following equation:

$$C_{if(m)} = S_i p'_{if}; \quad C_{ip(m)} = S_i p'_{ip} \tag{2.5}$$

Those values can then be substituted into the equation 2.3 to obtain a important equation:

$$J_i = \frac{D_i S_i\left(p'_{if} - p'_{ip}\right)}{\delta} \tag{2.6}$$

which is widely used to accurately and predictably rationalize the properties of permeation membrane and can guide one to design the permeation module and chose the operation parameters.

2.4 Summary

The conclusions of the literature review are listed as follows:

1. Research suggests that tailor-making films to yield any degree of permeability for any organic vapor is possible.
2. For the membrane environmental applications, by far, the most of studies were focused on using MIMS to analyze VOCs in water.
3. The most successful membrane material for use in the detection of organic compounds in aqueous solution is silicone rubber.
4. Literature investigation have been quite limited for membrane-GC application as well as the direct determination environmental significant compounds from air.
5. The solution-diffusion mode is used to explain and describe a permeation process by non-porous membrane.

CHAPTER 3

OBJECTIVES

The objective of this study is to develop air sampling techniques using a membrane permeator. In this approach the membrane is to serve as a selective barrier through which organic compounds will permeate selectively from air onto a measurement device. The membrane will be used in two different air sampling approaches. The first is sampling into a whole air sampler. Here the organic compounds will be preconcentrated by membrane permeator prior to analysis. In the other application, membrane will be used to continuously sample volatile organic compounds from air into a gas chromatograph for continuous on-line monitoring.

The focus of this research is two fold:

(1) Development of membrane permeation canister sampling for preconcentration of VOCs into a canister;

(2) On-line membrane extraction for direct introduction of VOCs from air emissions into a gas chromatography for continuous, on-line monitoring.

The objective of the first project is to explore the possibility of developing a membrane permeation based canister sampling device to selectively collect trace level VOCs from air. The VOCs will be preconcentrated into the canister via membrane permeation and interferences such as moisture will be reduced. The characteristics of sampling system, as well as the effects of operating parameters will be investigated.

For the second project: direct introduction of VOCs into a GC for on-line analysis, an on-line membrane extraction device coupled with a microtrap and gas chromatographic analysis will be studied. Preliminary study on this work was initialed by Ms. Xin Zhang. The scope of previous work will be expanded and the process will be studied in more detail and applied to determination of VOCs at parts per billion levels. In the study, the applicability of the on-line monitoring system in a real-world application will be also investigated by monitoring the emissions from an air toxic control device. In order to obtain both high permeability and selectivity, a composite membrane, microporous polypropylene hollow fiber coated with a thin layer of silicone, will be selected in this on-line monitoring study.

CHAPTER 4

SELECTIVE CONCENTRATION OF VOCs INTO A CANISTER USING A MEMBRANE PERMEATOR

(PART I: PERFORMANCE AND OPTIMIZATION)

4.1 Introduction

There is a need to improve techniques for collection and analysis of volatile organic compounds in ambient and work-place air. Traditional air sampling techniques include gas sample loops with valves [Jonsson, Vejrosta, and Novak (1982)], sample bags or containers such as canisters [Giannovario et al. (1976); Hamm and Warneck (1990)], and timed volumetric flow [Stephens (1989); Hancock et al. (1991)]. The sampling steps are followed by a concentration step that can involve impingers, cryogenic traps, or solid sorbent traps. These techniques are published as standard EPA methods referred to as the "TO Series" methods. These methods are quite effective in measuring VOCs in air. In method TO-1 and TO-2, a sorbent cartridge containing 1-2 grams of Tenax and carbon molecular sieve is used to trap VOCs from air. Then the cartridge is transferred to an analytical lab where the cartridge is placed in a thermal desorber apparatus. The VOCs are thermally desorbed in a flow of inert gas and transferred onto a cryogenic trap. The trap refocuses the analytes and injects them into a capillary column for high resolution chromatographic separation. In EPA method TO-14, a whole air sampler such as a canister is used to collect air samples. The canisters are then brought back to the lab for analysis which involves cryogenic preconcentration prior to GC or GC/MS analysis.

The sampling method using Summa passivated canisters has some advantages over sorbent traps [Hsu et al. (1991)]. Summa passivated canisters yield representative air samples. The chrome-nickel oxide layer coated on the inner metal surface of the canister deactivates the active sites, which increases the stability of many organic compounds and samples can be held for relatively long periods of time. Recently, silica lined canisters have been developed which are an improvement over the electropolished summa canisters. Moreover, the breakthrough of the volatile organic compounds which is a common problem for sorbent cartridges is not encountered in the canister samplers. Also, polymeric sorbents such as Tenax can degrade to form artifacts which interfere in trace analysis. Desorption efficiency of aromatic and higher molecular weight compounds can be quite low for strong adsorbents such as carbon molecular sieves which have high surface area and may bind aromatic compounds irreversibly. Another major advantage of canister sampling is that several subsamples from the same canister can be analyzed to obtain a measurement of precision, whereas, each sorbent trap can be analyzed only once. However, there are several limitations associated with canister sampling. Moisture from air can cause problems during GC or GC/MS analysis. Moisture freezes in the cryogenic trap and the capillary interface , thus reducing trapping efficiency for VOCs. Besides, moisture may cause a great deal of difficulty in the analysis of water soluble compounds such as alcohols, ketones, aldehydes, etc. Moreover, a canister collects "whole air" and provides no selectivity towards the VOCs, i.e. the organic compounds are not preconcentrated in the canister.

The objective of this study is to explore the possibility of developing a membrane permeation based canister sampling device to selectively collect trace level VOCs from air. The VOCs will be preconcentrated in the canister and interferences such as moisture will be eliminated. The characteristics of the sampling device, as well as the effects of operating parameters such as temperature, flow rate, pressure difference, sampling time were investigated in this project.

Membranes have been used as separation media in many processes such as gas separation, the recovery of the organic vapor from air streams, osmosis, dehumidification, etc. In recent years membranes have also been utilized in analytical techniques to separate organic compounds from complex air or aqueous matrix [Bauer and Solyom, (1994); Lapack and Lou, (1991); Silivon, et al. (1991); Kotiaho et al., (1991); Xu and Mitra, (1994); Yang et al. (1994); Melcher and Morabito, (1994); Mitra et al. (1996)] The membrane serves as a barrier for selective transmission of the analytes across it. In case of VOCs analysis, a membrane is selected such that organic compounds permeate selectively through the membrane leaving behind N_2, O_2, H_2O, and other components present in air.

Membranes may be classified as "porous" where separation occurs by selective diffusion through small pores, and "non-porous" where the analyte permeates through a polymeric membrane by an activated diffusion process, i.e., a combination of solubility and molecular diffusion. First the analytes dissolve into the polymeric membrane and then diffuse through it under a partial pressure (or concentration) gradient. The membranes currently used for analysis of organic compounds are non-porous polymers such as silicone. The permeation flux J_i of a compound i across the membrane is directly proportional to the permeability P_i, the partial pressure gradient of component i and is inversely proportional to the membrane thickness δ according to the equation:

$$J_i = \frac{P_i(p'_i - p''_i)}{\delta} \qquad (4.1)$$

where p'$_i$ and p"$_i$ represent the partial pressures across the membrane. This equation is widely used to describe gas permeation through membranes.

In general, permeation through the membrane is a complex process that involves chemical interactions, mass transfer, partitioning onto the membrane, and diffusion of the analyte through the membrane. The permeation process is sensitive to process variables such as partial pressure gradient, temperature, sample flow, etc. A more fundamental understanding of the sorption and permeation effects will help to gain further insight into the transport of organic compounds through membranes. Studies on diffusion, sorption and permeation of gases and some organic compounds in various polymeric membranes have been published widely in engineering literature. A review by Rigers in 1965 cited some 350 references [Rogters(1965)]. A more recent review on gas separation using polymeric membrane cited two hundred sixty two papers [Stern, (1994)] in which the relationship between membrane structure and permeability as well as selectivity was reviewed. Several studies have reported the permeability of VOCs through polymeric membranes especially silicone, however very few studies have dealt with the mechanism of permeation. Another shortcoming of these studies is that most of them have dealt with the transport behavior of pure compounds or at high concentrations. During air sampling trace concentrations (ppm to ppb levels) are encountered and much of this data can not be extrapolated to trace levels. Thus, another objective of this study is to develop a better understanding of membrane permeation at trace levels.

4.2 Experimental Section

A schematic diagram of the Membrane Permeator Canister Sampling System (MPCS) is presented in Figure 4.1. The air sample containing trace level volatile organic compounds as well as component like N_2, CO, O_2, and moisture passed through a polymeric membrane module containing membrane fibers. The VOCs selectively migrated across the membrane into a evacuated canister. After sample was collected by the MPCS system, VOCs were analyzed by GC or GC/MS. Three different membrane module designs were tested: "flow-over", "flow-through" and flow through with N_2 stripping (Figure 4.1). In a "flow-over" configuration, the air sample passed on the outside of the membrane and a canister was connected to the inside of membrane. In the "flow-through" configuration, the sample passed through a hollow fiber membrane while the VOCs and some air permeated across the membrane and diffused into a evacuated canister. In the "flow-through" configuration nitrogen was also used as a stripping gas.

The canisters used in the study were Summa passivated canisters from Scientific Instrumentation Specialists (Moscow, ID). Gas standards were supplied by Alphagaz (Morrisville, PA, USA) containing 1 ppm of benzene, trichloroethane, toluene, ethylbenzene, 164 ppm sulfur dioxide, 75 ppm CO, 9.27% CO_2, 10.9% O_2, and balance nitrogen. Polar VOC gas standard containing twenty oxygenated polar compounds was also obtained from Alphagaz. Gas samples were also prepared in 6 L canisters or 13 L cylinder. This was done by injecting pure liquid organic compounds and filling the cylinder/canister with a dry zero grade air to a predetermined pressure following the method published by Hsu [Hsu et al. (1991)]. The concentrations of the laboratory made

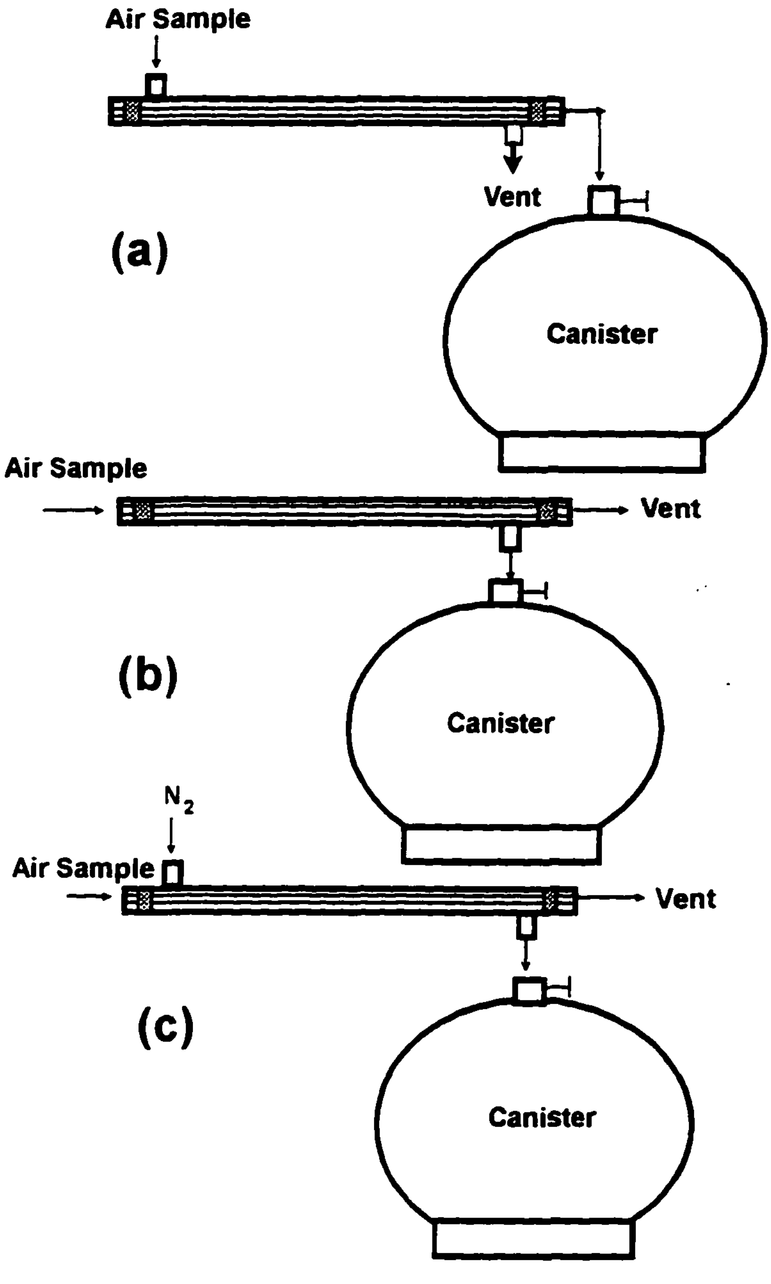


Figure 4.1 Membrane permeator for sampling of VOCs: (a) the "flow over" configuration; (b) the "flow through" configuration; (c) "flow through" with nitrogen stripping.

standards were verified running the certified gas standards. All chemicals used in this research were chromatographic grade and purchased from Fisher Scientific.

The membrane material used in this study was mainly poly (dimethylsiloxane) elastomer, or silicone rubber as it is commonly called. The dimension of fiber was 0.305 mm I.D. x 0.635 mm O.D. and obtained from Dow Corning Corporation (Midland, MI, USA). In some investigations, a composite membrane (0.206 mm I.D. x 0.260 mm O.D.) was used, which supplied by Applied Membrane Technology, Inc. (Minnetonka, MN, USA). This membrane had 1 μm siloxane film on the surface of a porous polypropylene support material. The membrane module was designed to be equipped with a single or multiple membrane fibers. For constructing a single fiber membrane module, the end of the hollow fiber was immersed in toluene or xylene for about 5 to 7 minutes first, and then, the membrane was carefully slipped over a narrow bore stainless steel tubing (0.381 mm outer diameter). After toluene or xylene evaporated, the fiber shrank and formed a tight fit. Then, the fiber connected to the thin steel tubing was encased in a piece of 1/8" tubing and the connection points were sealed using silicone glue. The module with multiple fibers was constructed from a piece of 1/4" tubing with as many as twenty hollow fibers going through it. The ends of the module were sealed using epoxy which formed a strong bond that could endure relatively high pressure.

A Hewlett-Packard Model 5890 Series II gas chromatography, (Hewlett Packard Inc., Avondale, PA) equipped with a flame ionization detector was used for analysis. A 30 m long, 0.53 mm od x 0.32 mm id DB-624 column with 3.0 μm thick stationary phase was used for separation (J & W Scientific, Folsom, CA, USA). The data acquisition from the GC was done using HP 3365 Chemstation. The general operating conditions for

GC/FID were as follows: Hydrogen 25-35 ml/min, air 300-325 ml/min, Nitrogen make up gas 15-25 ml/min, and carrier gas 5-10 ml/min. Oxygenated compounds were analyzed using GC/MS (HP GC: Model 5890 series II, HP MSD: model 58999) with a 75 m long DB-5 column and data acquisition and interpretation were done by RTE-A.

4.3 Results and Discussion

4.3.1 The Performance of MPCS System

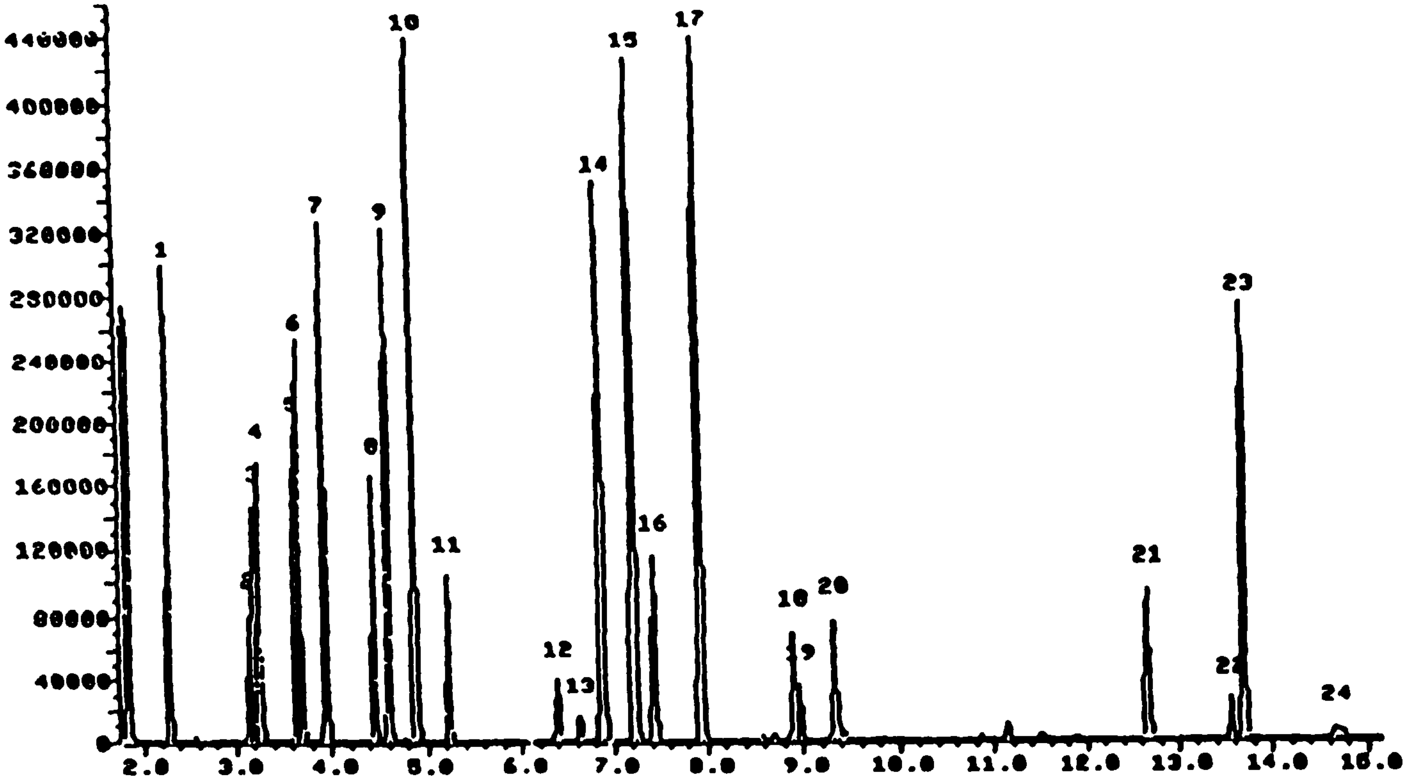
4.3.1.1 Enrichment of VOCs: The performance of the MPCS sampling system was demonstrated by selectively collecting seventeen oxygenated compounds from a standard air sample. These compounds were chosen because they are most difficult to analyze by canister sampling. This standard contained 2300 ppbv Acetaldehyde, 1300 ppbv Acetonitrile, 1400 ppbv Acrylonitrile, 970 ppbv Bis (2-Chloroethyl) ether, 210 ppbv Chlorobutanol, 300 ppbv Chloromethyl methyl ether, 340 ppbv Chloromethyl Oxirane, 1100 ppbv Dimethoxyl methane, 2800 ppbv 1,4-Dioxane, 1800 ppbv Ethyl Acrylate, 1700 ppbv MTBE, 460 ppbv Propylene Oxide, 1300 ppbv Propionaldehyde, 1700 ppbv MEK, 1400 ppbv Carbon Disulfide, 1900 ppbv MIBK, and 1900 ppbv Vinyl Acetate. During the experiment, the air sample passed through a hollow fiber membrane module ("flow-through" configuration) at a flow rate of 20 ml/min while permeated VOCs were collected by an evacuated canister. Another sample was collected by sampling the gas standard directly into the canister without going through the membrane. Both sets of canisters, with and without membrane were analyzed using a canister analysis (standard EPA method TO 14 approach) system coupled with GC/MS detection. Fluorobenzene was used as the internal standard, 2-Bromochloropropane and 4-BFB were used as surrogates. The chromatogram of the VOCs is presented in Figure 4.2. The analysis of both sets of canisters is presented in Table 4.1. The results clearly demonstrate that MPCS system concentrated the organic compounds in the canister. The concentrations after membrane permeation are considerably higher. Concentration in the canister can be higher than the outside air because the mass transfer is brought about by the partial pressure gradient across the membrane according to Equation 4.1. Here, the vacuum in the canister provided driving force required for sample preconcentration.

The stability of VOCs after membrane permeation was also investigated. After almost of one month, the sample in the same canister was analyzed again and then the results were compared with the results obtained originally. The concentrations of the VOCs after one month and the relative standard deviations for those two runs are also listed in Table 4.1.

In order to quantitate the preconcentration effect of organic compounds in the canister, the parameter enrichment factor (%E) was used. The enrichment factor is defined as:

$$Enrichment\ factor\% = \frac{Concentraion\ of\ permeated\ VOC\ in\ the\ canister}{Concentration\ of\ VOC\ in\ feed\ air} X100 \qquad (4.2)$$

The enrichment factors for the components in Figure 4.2 are presented in Table 4.1. It is seen that the enrichment factor was different for different compounds and varied anywhere from 230% to 710%. The enrichment factor depends upon the selectivity of the membrane for a certain component with respect to air components such as N_2. Experimental results demonstrate that the silicon membrane used in this experiment had a high selectivity resulting in a high enrichment factor. Thus it may be inferred that



1. Acetaldehyde 2. Propylene Oxide 3. Acetonitrile 4. Propionaldehyde 5. Dimethoxylmethane
2. Acrylonitrile 7. Carbone disulfide 8. MTBE 9. Vinyl acetate 10. MEK
11. IS 12. BZF 14. Ethyl acrylate 15. 1,4-Dioxane 16. Chloromethyl oxirane
17. MIBK 18. SS_1 19. Chloromethyl methyl ether 20. Chlorobutanol
21. SS_2 24. Acetophenone 23. Bis (2-Chloroethyl) ether

Figure 4.2 The chromatogram of polar and oxygenated VOCs collected using the MPCS system. The sample collected with a feed pressure of 40 psi, the sample flow rate was 20 ml/min, and the temperature of the membrane module was 55 to 60 0C. The analysis was performed by PACE Environmental Laboratories (SoCal Division, Camarillo, CA).

Compounds	Standard Concentration (ppbv)	MPCS Concentration (ppbv)	Concentration after 1 month	RSD%	Enrichment Factor%
Acetaldehyde	2300	7360	7452	0.9	320
Acetonitrile	1300	4600	3184	26	350
Acrylonitrile	1400	6440	6164	3.1	460
Bis(2Chloroethyl)ether	970	3300	3146	3.4	340
Chlorobutanol	210	874	750	8.6	420
Chloromethyl methyl ether	300	690	754	6.3	230
Chloromethyl Oxirane	340	2400	2075	10.3	710
Dimethoxylmethane	1100	3100	3300	4.4	280
1,4-Dioxane	2800	11500	12800	7.6	410
Ethyl Acrylate	1800	7400	6390	10.4	410
MTBE	1700	4690	3988	11.4	280
Propylene Oxide	460	1900	1870	1.1	410
Propionaldehyde	1300	5060	4960	2.3	390
MEK	1700	6900	6700	2.1	410
Carbone disulfide	1400	6440	5911	6.1	460
MIBK	1900	6440	6279	1.8	340
Vinyl acetate	1900	7360	7153	2.5	390

Table 4.1 The enrichment factor of oxygenated and polar VOCs using MPCS system

semipermeable membrane acts as a separator and a concentrator. MPCS of oxygenated compounds is particularly relevant because, these compounds are more difficult to analyze by conventional canister methods and have relatively higher detection limits compared to hydrocarbons. The preconcentration leads to lower detection limits

Moreover, according to many environmental lab experience, the holding time for non-oxygenated VOC sample is seven to fourteen days, beyond that, these compounds may be not stable. From Table 4.1, it is seen that after one month, the tested compounds were still stable and the concentrations were almost as same as one month earlier. The RSD% for all compounds, except Acetonitrile, were less than 15. The experimental results indicate that some inferences which would cause the degradation of the polar and oxygenated VOCs were removed by the membrane permeator, which suggests that the membrane-canister sampling system is potentially an excellent sampling technique for collecting and storing the polar and oxygenated VOCs.

4.3.1.2 The Relationship between Enrichment Factor and Membrane Selectivity:

Experimental results demonstrated that trace level VOCs can be concentrated from air matrix by membrane permeation process. The enrichment factor is determined by two factors. The first is membrane selectivity and the second is the pressure ratio Φ across the membrane. The overall selectivity of a polymer membrane toward two different penetrant gases, namely, i and j, is commonly expressed in terms of an "ideal" separation factor, $\alpha_{i/j}$, [Stern, (1994); Peinemann, et al. (1986); Baker and Wijmans, (1994)]:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \left[\frac{D_i}{D_j}\right] * \left[\frac{S_i}{S_j}\right] \qquad (4.3)$$

The factor $\left[\frac{S_i}{S_j}\right]$ is the ratio of the Henry's law sorption, or solubility, coefficients of the two pemeants and is known as "solubility selectivity", which reflects the relative condensability of the two pemeants on the membrane. The solubility coefficient is a measure of the energy needed for the permeant to be sorbed by the membrane and increases with the increasing condensability of the permeant. Therefore, the solubility selectivity is normally significantly higher than 1 due to the high condensability of organic vapors compared to oxygen and nitrogen. The factor $\left[\frac{D_i}{D_j}\right]$ is the ratio of the diffusion coefficients (or diffusivity coefficients) of the two permeants and is commonly called "diffusivity selectivity" or “mobility selectivity”. To a certain extent the diffusion coefficient is a function of the size of the molecule. Consequently it depends upon the size of the VOCs molecules relative to N_2 and O_2. The mobility selectivity is always less than 1 for VOCs with respect to air because a large organic molecule interacts with more segments of the polymer chain than small molecules. This leads to a decrease in its diffusion coefficient. It is the balance between the solubility selectivity and the mobility selectivity that determines whether or not a membrane material is selective towards an organic compound over air.

The second factor which will affect the enrichment of an organic compound is the pressure ratio Φ, across the membrane defined as:

$$\Phi = \frac{p'}{p''} \tag{4.4}$$

where p' is the total pressure in the feed side of the membrane and p'' is the total permeate pressure. The relationship between these parameters and the membrane selectivity can be derived from the Fick's-law:

$$\textit{Transmembrane flux } J = \left(\frac{\textit{permeability}}{\textit{effective membrane thickness}} \right) \textit{pressure difference}$$

For a mixture i and j system,

$$J_i = \frac{P_i(p'_i - p''_i)}{\delta} \tag{4.5}$$

$$J_j = \frac{P_j(p'_j - p''_j)}{\delta} \tag{4.6}$$

where P_i and P_j are the permeabilities of species i and j, δ is the membrane thickness, and p'_i, p'_j *and* p''_i, p''_j are the partial pressures of the two species in the feed and permeate side , respectively. The total pressures on both side of the membrane can be obtained by the following equations:

$$p' = p'_i + p'_j \tag{4.7}$$

$$p'' = p''_i + p''_j \tag{4.8}$$

and the concentrations for each species on both side of the membrane can be calculated as follows:

$$\textit{concentraiton} = \frac{\textit{partial pressure}}{\textit{total pressure}} \tag{4.9}$$

Combining the equations from 4.1 to 4.9 with

$$\frac{J_i}{J_j}=\frac{C''_i}{C''_j}=\frac{C''_i}{1-C''_i} \tag{4.10}$$

a relationship between membrane selectivity and pressure ratio is obtained:

$$C''_i=\frac{\Phi}{2}\left\{C'_i+\frac{\alpha-1+\Phi}{\Phi(\alpha-1)}-\sqrt{\left(C_i+\frac{\alpha-1+\Phi}{\alpha-1}\right)^2-\left[\frac{4\alpha C''_i}{(\alpha-1)\Phi}\right]}\right\} \tag{4.11}$$

where, C''_i and C''_j are the concentrations of component i and j in the permeated side. From the equation 4.11, it is seen that at high pressure ratios, i.e. relatively low permeate vacuums, when $\alpha >> \Phi$, selectivity can be calculated as:

$$\alpha=\frac{C''_i/(1-C''_i)}{C'_i/(1-C'_i)} \tag{4.12}$$

where C'_i is the concentration of component i in the feed side of the membrane. Since we are dealing with trace concentration, the terms $(1-C''_i)$ and $(1-C'_i)$ are close to 1 and

$$\alpha=\frac{C''_i}{C'_i} \tag{4.13}$$

Thus enrichment factor is equal to selectivity α.

Reported values of selectivity are much higher than the enrichment factor presented in Table 4.1. For example, Blume and co-workers reported that the ratio of the permeabilities of toluene to nitrogen was about 5200 [Blume, Schwering, Mulder, and Smolders, (1991)]. In another investigation [Baker et al. (1987)], the overall selectivities of the membranes were found to vary from 100 to 10,000 depending on the organic compounds and polymer materials. More recently, Baker and Wijmans reports that the selectivities of composite membranes for organic vapors over air are typically of the order 20-100 [Baker and Wijmans, (1994)]. In all these studies, selectivity was determined using pure compounds. Permeation flux of the different gas species were measured separately, and then selectivity was calculated as the ratio of the permeability of pure species. These results can not be extrapolated to air sampling issues being addressed here as trace concentrations are encountered in this situation. At high organic vapor concentrations sorption onto the membrane material can cause significant swelling which, in turn, increases the permeation rate. Therefore, the membrane selectivities calculated from pure species are expected to be significantly higher than enrichment factors measured here.

Moreover, from a mechanistic viewpoint, in these studies, both the organic compounds and air (nitrogen) had the same probability of coming in contact with the membrane since measurements were carried out separately for each species. In contrast, at ppm to ppb concentration levels, the probability of contact of an organic molecule with membrane is significantly lower than the air molecules present at high concentration. Consequently, the enrichment factor based on trace level permeants in an air matrix was significantly less than the membrane selectivity based on pure gas measurements. It also follows that in the equation 4.12, assuming component i is a volatile organic compound and is present in the ppbv level, and component j is the air matrix, air will be present in orders of magnitude higher concentration on both sides of the membrane compared to the trace level organics, irrespective of the intrinsic membrane selectivity. Therefore, at such condition, the equation 4.11 can be reduced to the equation 4.13, which is similar to the expression for enrichment factor (Equation 4.2).

4.3.1.3 Linearity of MPCS System Response: Since a new sampling method is being developed it is necessary to determine whether the concentration of permeated sample truly represents the concentration of air being sampled. Experiments were done to see if the concentration in the canister after membrane permeation was proportional to the concentration in the air being sampled. Benzene, Trichloroethane, Toluene, and Ethylbenzene were used in the concentration range of 10 ppb to 1000 ppb. The experimental results are presented in Figure 4.3. From Figure 4.3, it is observed that the concentration of VOCs after membrane extraction increased proportionally with increasing VOCs feed concentration and this linear relationship was exhibited over a wide dynamic range. This is because the permeation rate is directly proportional to the sample concentration and varies from compound to compound.

As noted in the introduction, transport through a polymeric membrane can be described by a solution-diffusion process, whereby the permeability, P, of mass transfer is the product of the diffusion coefficient D, and the solubility coefficient S as follows:

$$P = D * S \tag{4.14}$$

For the case of an organic compound permeation, it can be seen that concentration dependent sorption has a major influence on the overall transport characteristics of the membrane and leads to high organic compound permeability. However, the relationship between permeation rate and sample concentration can be linear or not, depending the how high concentration is, in a sample.

Fick's law requires that D be independent of the concentration of permeant in the membrane and Henry's law constraint that requires S to be independent of the pressure or activity of the permeant in the phase in equilibrium with the membrane. From the

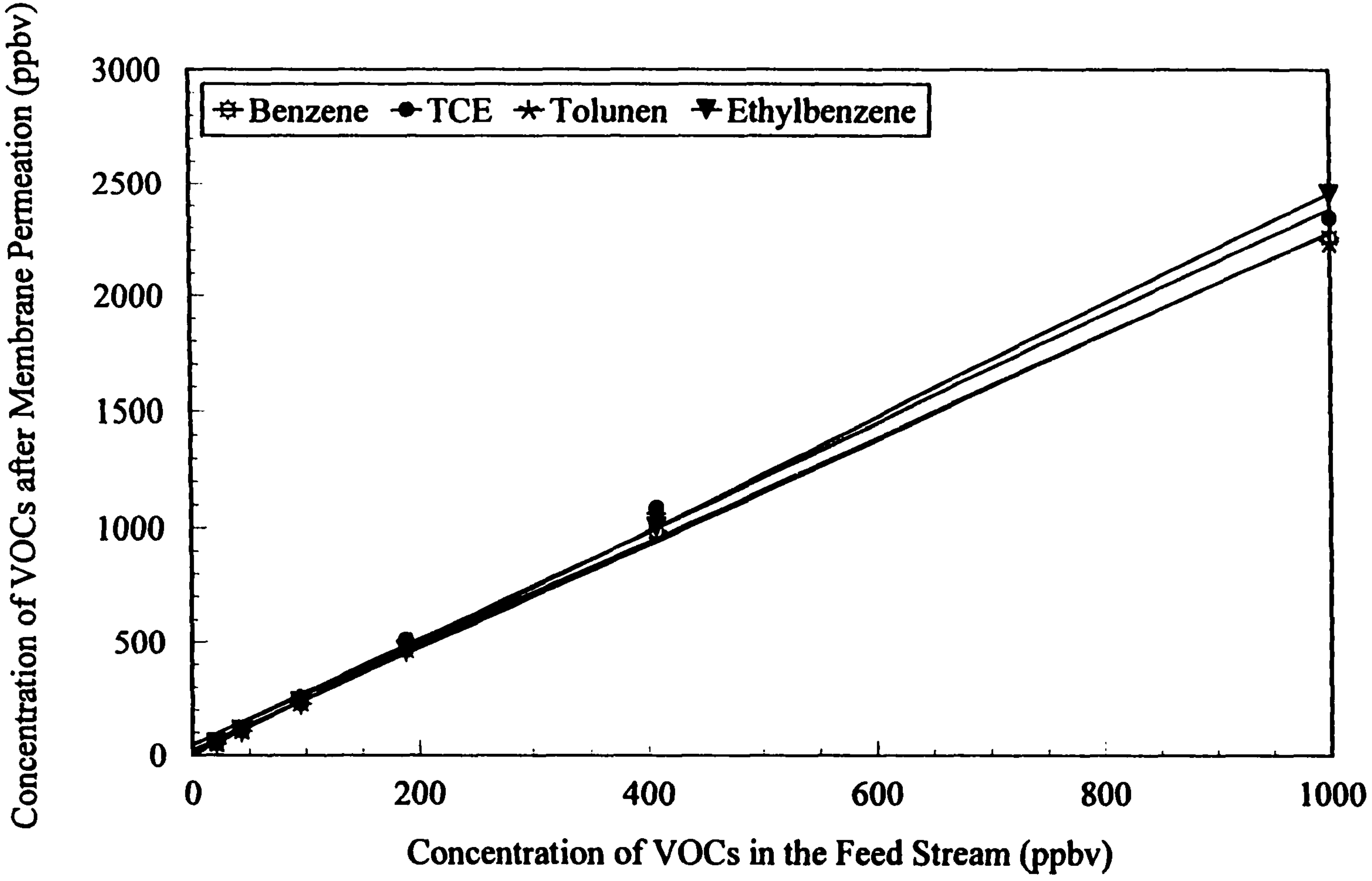


Figure 4.3 The linear relationship between permeation and concentration change in the feed stream using MPCS system.

equation 4.14 it is seen that if Fick's law and/or Henry's law are not beyond, then the permeability P will also be dependent on the partial pressure or activity of the permeant.

At high concentration, since the permeation of organic compounds through the rubbery polymers do not follow Henry's law and Fick's law, the permeability is not constant. This situation is due to the solubility increasing at a rate that faster than the rate of increase of the partial pressure (concentration) and, likewise, the rate of diffusion. Consequently, the rate of permeation increases faster than linearly with the pressure difference and is dependent not only on the pressure differential but also on the absolute partial pressure.

For a low concentration permeation process, however, Henry's law and Fick's law are obeyed. Thus diffusion coefficient and solubility coefficient (Henry's law constant) are constant which are in agreement with the experimental results and other publications [LaPack et al. (1990); Harland et al. (1987); Winston Ho, and Sirkar, (1992); Yan and Pawliszyn, (1993)]. At a low concentration, a permeation process can be described by Fick's law and for a hollow fiber membrane, Fick's law gives:

$$J = 2\pi l D \frac{(C_1 - C_2)}{\ln r_o - \ln r_i} \tag{4.15}$$

where l is the length of the hollow fiber membrane, C_1 and C_2 are the concentrations of permeant in the high- and low pressure surfaces of the membrane, respectively, and r_o and r_i are the outer and inner radii of the hollow fiber, respectively. LaPack [LaPack, Tou, and Enke (1990)] used a distribution ratio:

$$K = \frac{C_1}{C*} \tag{4.16}$$

to modify the Fick's equation and provided a more generalized form for explaining the relationship between the permeation response and the concentration of the sample:

$$J = \frac{2\pi dDKC*}{\ln r_o - \ln r_i} \tag{4.17}$$

where K is the pressure-dependent distribution ratio, and C* is the concentration of the permeant in the sample. Form the equation 4.17, it is shown that at a given temperature and pressure, the dimension constant, $\frac{2\pi d}{\ln r_o - \ln r_i}$, and the permeability, $P = DK$, are constants, so that the permeation rate is directly proportional to the sample concentration which is consistent with the experimental results reported herein (Figure 4.3).

This linear relationship also indicates that the relationship between enrichment factors and the concentrations of VOCs should be linear. Experimental results agreed with this inference and are presented in Figure 4.4. Figure 4.4 shows that the linear relationship existed and the enrichment factors slightly increased with increasing the initial concentration of VOCs. This linear relationship can be used to calculate the actual concentrate of an organic compound in a unknown sample.

It should be noted that, on the one hand, the permeation is linear when the concentration is low; on the other, non-linear when high. This study is applied to ambient air samples in which the concentrations of VOCs are low so that analytical accuracy is optimized because a linear relationship exists.

4.3.1.4 Moisture Removal: Moisture is a serious problem when canisters are used to sample air. During analysis, when VOCs are concentrated in a cryogenic trap, moisture freezes and clogs the trap and capillary interface. As a result, only a small volume of air

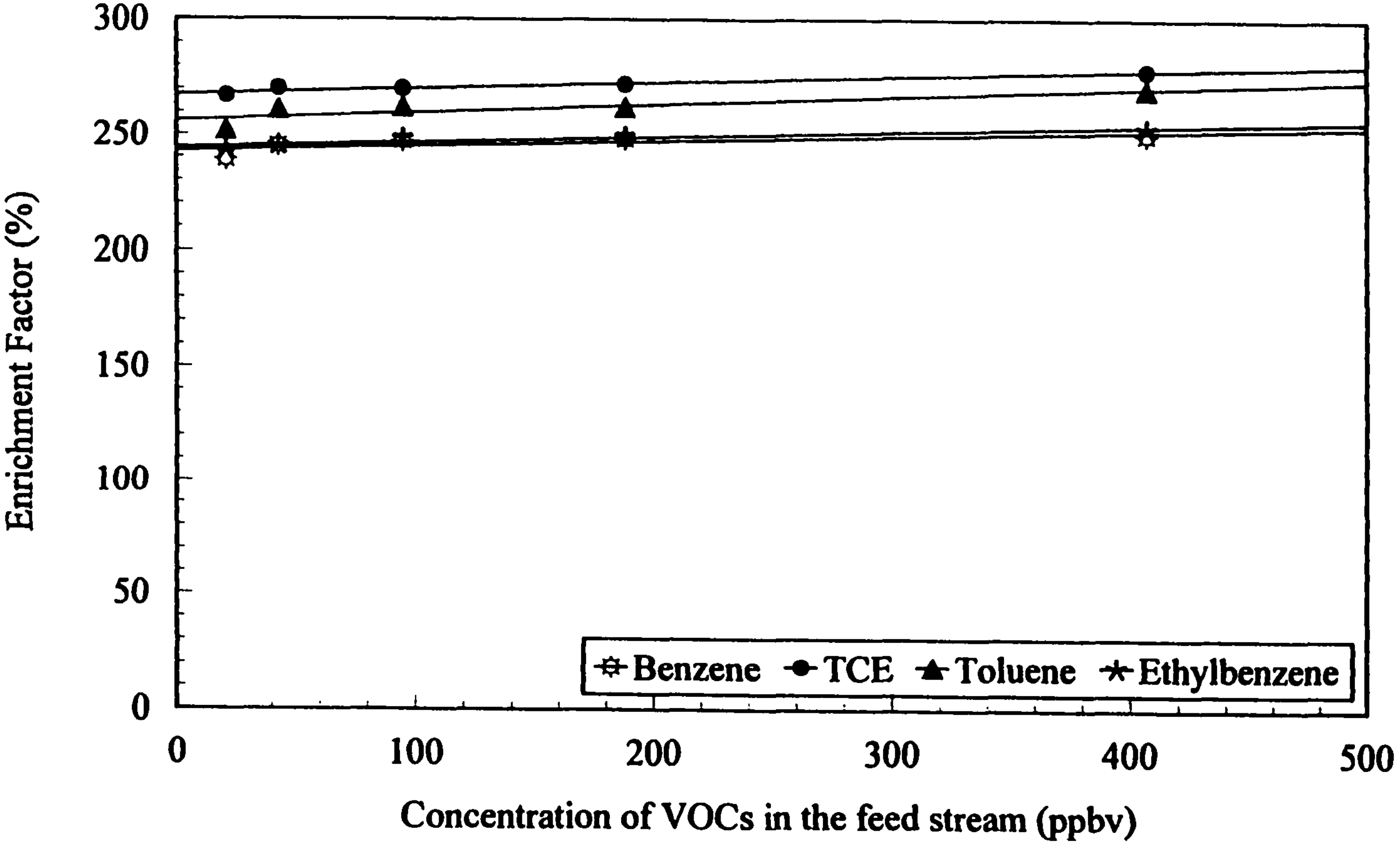


Figure 4.4 The effect of the concentration of VOCs in the feed stream. The pressure in the feed side of the membrane was 40 psi, and the temperature of membrane module was room temperature.

can be sampled from the canister prior to GC analysis. Moisture also causes difficulties in the analysis of water soluble compounds such as some oxygenated and polar analytes as they tend to dissolve in water if a cold trap is used to condense the moisture. When nafion dryer is used to remove moisture during the canister analysis, polar compounds such as alcohols and ketones are lost along with moisture.

The investigation for moisture removal using membrane permeator was carried out with humidified samples containing 47% moisture. Such high concentration may be encountered air samples from an emission source, such as industrial stack. Experiments were done by flowing the humidified air sample through the membrane and collecting the permeant in the canister. The inlet air stream as well as the permeate stream was analyzed for moisture using a GC with a thermal conductivity detector. Experimental results are presented in Table 4.2. For inlet stream with 47% moisture, the moisture content in the sample after membrane extraction decreased to 0.59%. This shows that 98.7% of the moisture was removed by membrane permeator.

Table 4.2 Moisture removal using a membrane permeator

Moisture content in the air sample	47%
Moisture content in the canister (after membrane extraction)	0.59%
Moisture removal by the membrane-canister sampling system	98.7%

The silicone or polydimethyl siloxane membrane used in this study is highly permeable to organic compounds, but relatively impermeable to water due to its hydrophobic nature. Thus the membrane permeator acts as a barrier that allows the selective diffusion of VOCs and the elimination of the water.

4.3.2 Optimization of the Experimental System

4.3.2.1 Effect of the Membrane Module Configuration: The majority of gas separation membranes are non-porous polymers. The modules are made either from flat sheet or hollow tubular fibers. A long roll of flat sheet membrane can be constructed into a spiral-wound module or assembled in plate-and-frame configurations. Hollow fibers have an advantage that they provide high packing densities by providing large surface area per unit volume. The comparison of different module designs is given in Table 4.3.

Table 4.3 Comparison of different module designs [Prasad, et al., (1994)]

Attribute	**Plate and frame**	**Spiral wound**	**Hollow fiber**
Area Packing density [m^2/m^3 (ft^2/ft^3)]	100 - 660 (30 - 200)	300 - 3000 (100 - 1000)	6500 - 20,000 (2000 - 6000)
Min. Skin Thickness ($\overset{0}{A}$)	500	500	500 - 1000
Flow Distribution or Pattern	Fair	Moderate	Good
Pressure Drop	Low	Low	Low-shell side Med.-bore side

Hollow fibers are small tubes that have outer diameters ranging from as little as 50 microns to over 500 microns. There are two basic membrane module designs for hollow fibers, namely, “flow-over” and “flow-through”. The “flow-over” module design allows the air sample to flow over the exterior of the fiber while the interior of fiber is exposed to the vacuum of the canister. Alternatively, the "flow-through" involves the air sample passing through the interior of the fiber while the exterior surface of the fiber is exposed to the evacuated canister. Both the "flow-over" and "flow through" membrane configurations were tested in this study for collecting 200 ppbv Toluene in the air sample and results are presented in Figure 4.5 and Table 4.4. Nitrogen, as a stripping gas at a low flow rate 1 ml/min, was also tried in a flow through configuration (Table 4.4 and Figure 4.1).

Table 4.4 The effect of the membrane module configuration on enrichment factor

Module configuration	**Flow-through**	**Flow-over**	**N2 as stripping gas (flow-through)**
Enrichment factor%	450	435	101

The purpose of using nitrogen as a stripping gas was to see if it could remove the equilibrium limitations and increase the permeation rate of VOCs. However, the experiment results showed that there was no enhancement the enrichment factor. The stripping gas diluted the VOCs in the canister offsetting any enhancement in permeation rate. From Table 4.4, it is observed that the enrichment factor 450% for "flow-through" configuration was almost the same as for the "flow-over" design: 435%. This may be due to that the permeation of the air matrix is also affected by the effective membrane area.

However it was noted that the rate of permeation was faster in the flow through configuration. When experiments were done by collecting samples for a fixed period of time, significantly larger quantities of VOCs were collected. In general higher Reynolds

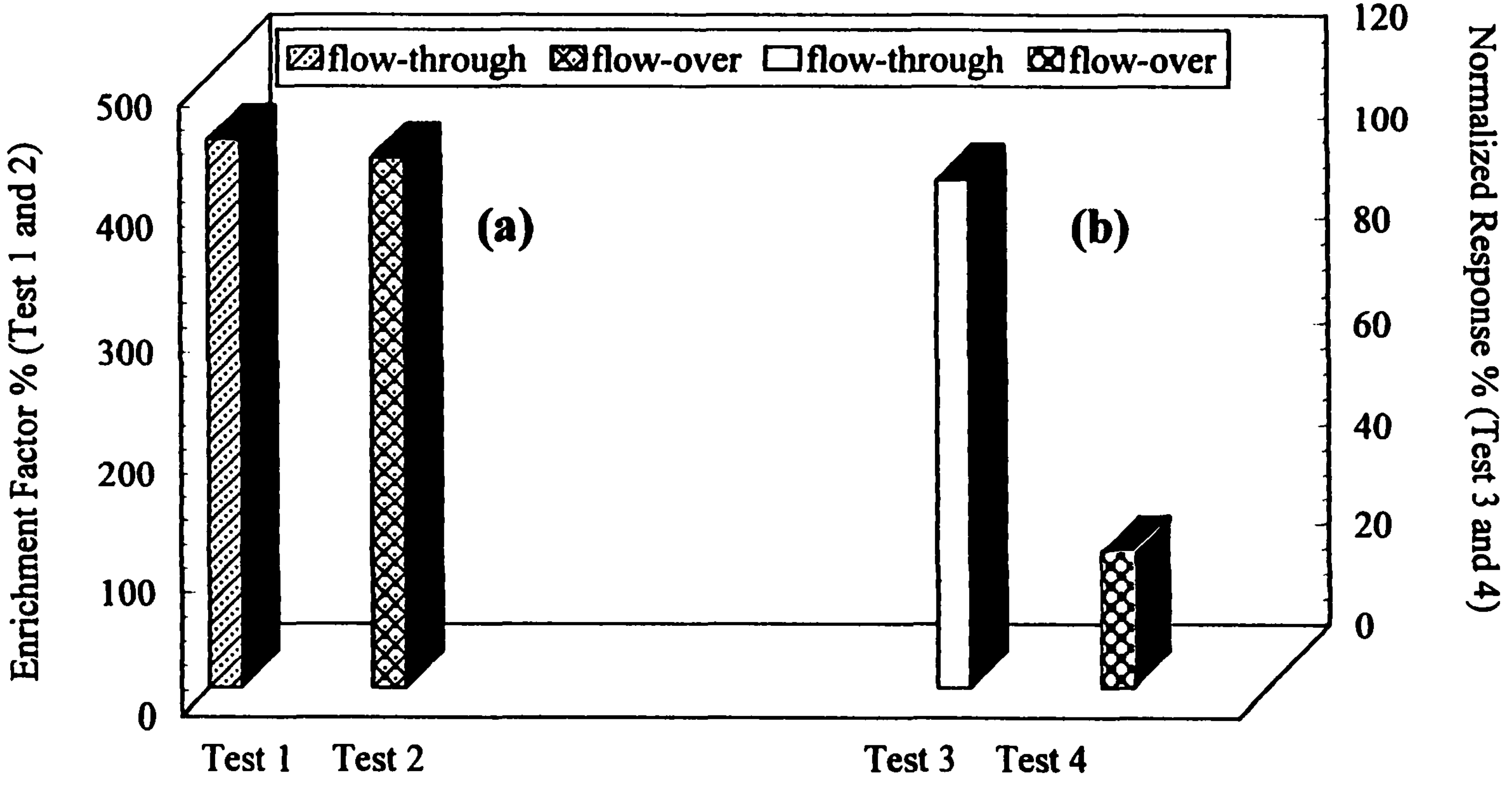


Figure 4.5 The effect of the membrane module configuration: (a) samples collected using MPCS system; (b) The concentration of VOCs in the outlet of membrane module was directly analyzed by GC. The tested VOC was 200 ppbv Toluene.

numbers $\left(\frac{dv\rho}{\mu}\right)$ are achieved in the flow through configuration resulting in faster mass transfer. In addition, the higher flow rate may cause the soft membrane fibers to collapse in the flow-over membrane module, thereby decreasing the effective membrane area. To determine which configuration has a higher rate of permeation, experiments were done by connecting the outlet of the membrane module directly to a GC and measuring the response at steady state. The experimental results of the GC response are also presented in Figure 4.5. It was found that the rate of toluene migration was almost four times faster in the flow through configuration than the flow over configuration. Considering all these factors, the flow through configuration without the N_2 stripping was chosen for the rest of the study.

It is interesting to see the difference in these two configurations is not as significant as has been reported in water analysis studies [Lapack et al. (1990); Shoemaker (1993)]. Lapack et al. who conducted experiments comparing the "flow-over" and the "flow-through" configurations for water sample, reported an almost 50-fold greater response using the "flow-through" rather than the "flow-over" configuration. This enhancement may be attributed to higher linear velocity encountered in the "flow-through" configuration. Higher velocity minimizes the formation of an analyte-depleted aqueous boundary layer at the membrane surface, resulting in improved mass transfer that lowers the response times and increases. In the case of air sampling, since air has a larger diffusivity and does not easily form a thick boundary layer, the mass transfer will much faster than in water.

4.3.2.2 Effect of the Sample Flow Rate: The effects of the sample linear velocity on the enrichment of VOCs using MPCS system was investigated and the results are presented in Figure 4.6. It is expected that higher flow rate will increase mass transfer across the membrane, that is, the amount of VOCs permeating through the membrane will increase with increase in sample flow rate. To see the effect of flow rate only on VOCs permetion, the membrane permeator was connected directly to a GC and the permeated VOCs stream was analyzed on-line. The experimental results for on-line measurement are presented in Figure 4.7. Both tests: using MPCS and on-line were carried out at room temperature and the feed pressure was 40 psi. As expected, as the flow rate increased, the permeation rate increased, thus increasing the GC response. At higher flow rates, the response began tapering off to a constant value.

Figure 4.6 shows results from experiments using the MPCS system where the air sample was allowed to flow at different velocities. Initially, the enrichment factor increased with flow rate, but beyond a linear velocity of approximately 300 cm/sec, the enrichment factor more or less stayed constant. This was true for all the different compounds studied. At very low rates, very little sample comes into the membrane. Consequently collection of VOCs is limited. Once N_{Re} of approximately 60 (linear velocity: 300 cm/sec.) was reached, the process was limited by rate of permeation rather than availability of sample.

Comparing Figure 4.6 and 4.7, it is seen that although the both enrichment factor using MPCS and GC response using on-line system were increased with increasing sample linear velocity, the increasing magnitude was different for two tests. The GC response increased with increased flow rate over a wider flow range than enrichment

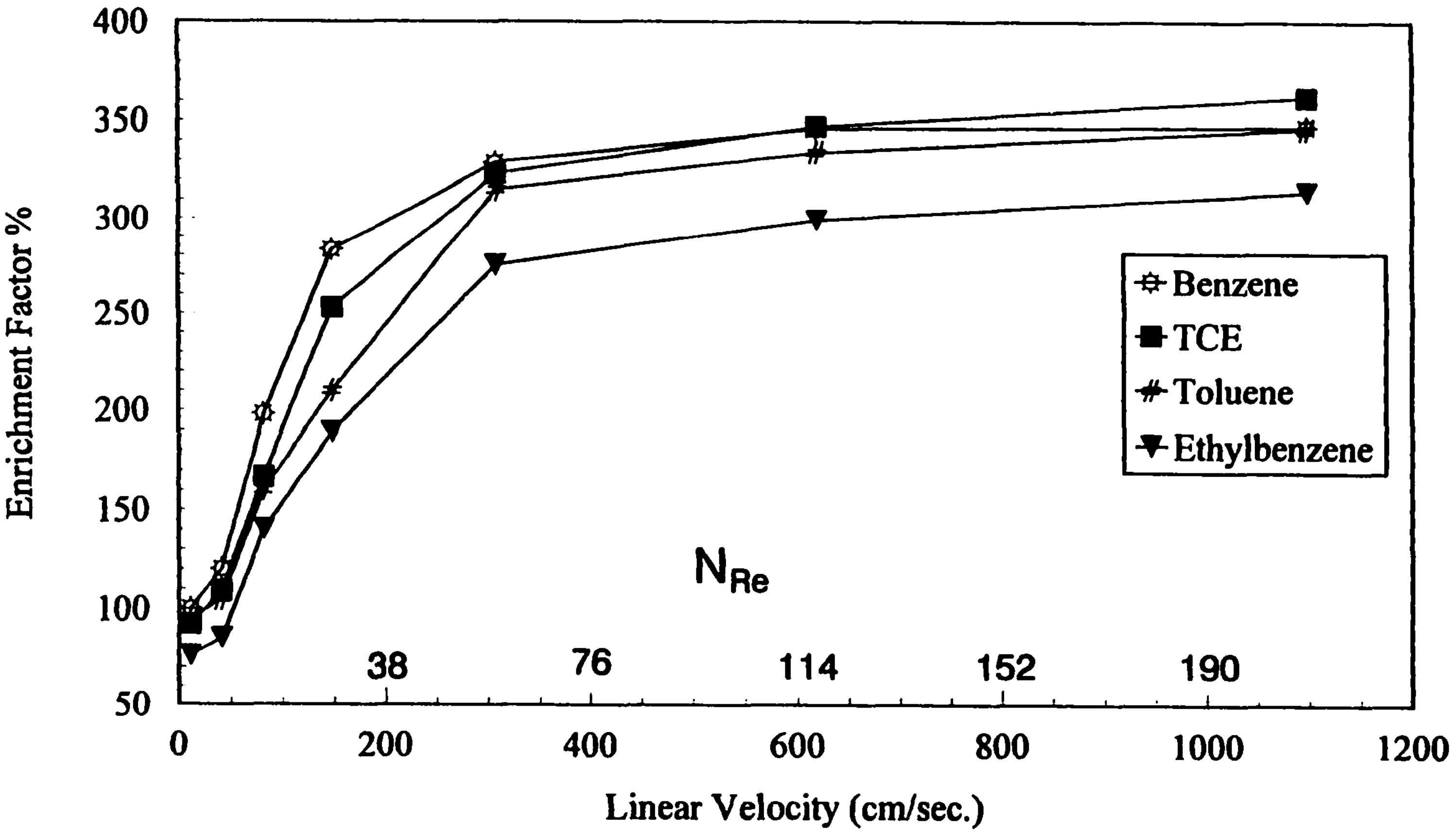


Figure 4.6 The effect of sample flow on enrichment factor. The feed side pressure was 40 psi and room temperature.

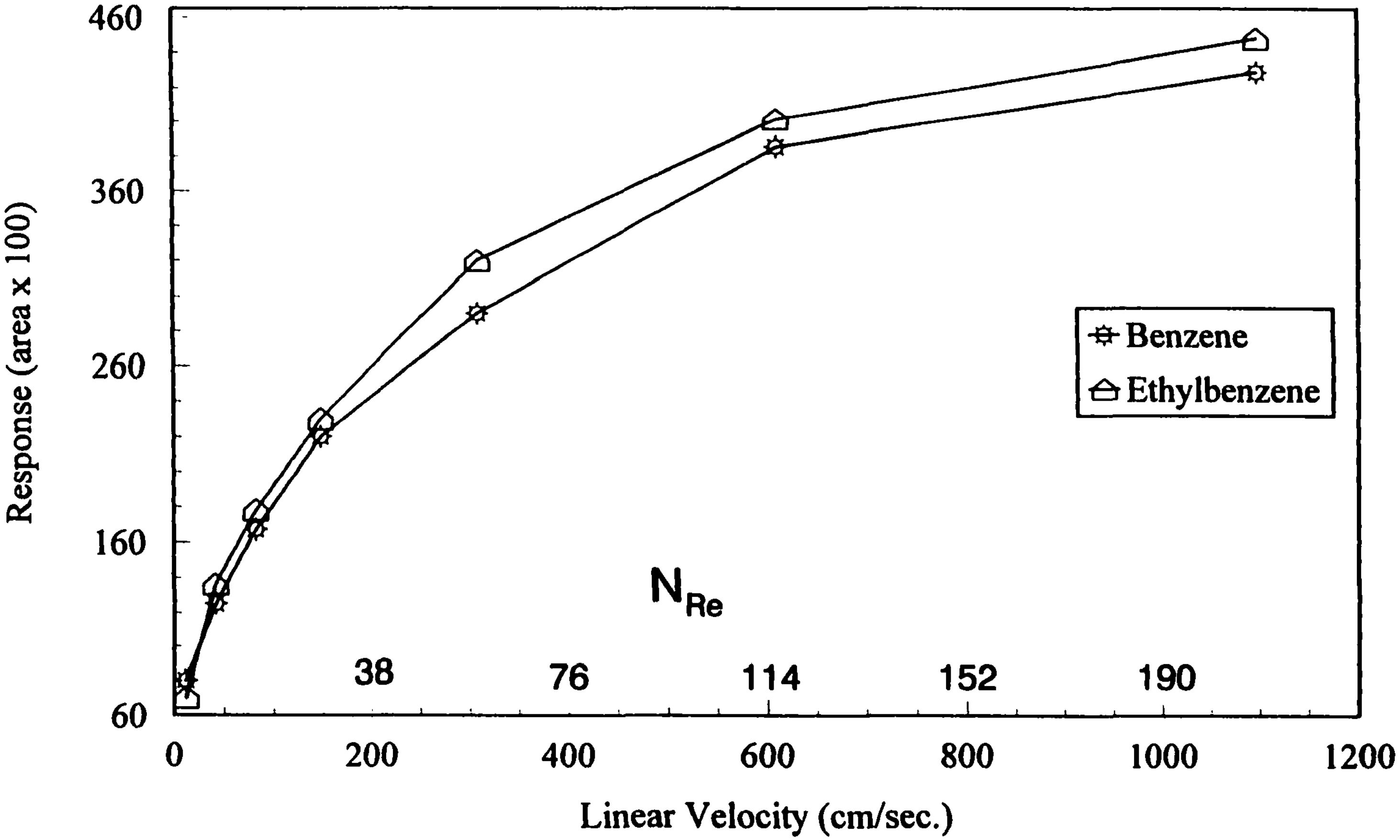


Figure 4.7 The effect of sample flow. The pemeated VOCs after membrane permeator was analyzed on-line. The pressure in the feed side was 40 psi and collecting sample at room temperature.

factor study. In other words, although a significant gain in the system sensitivity was obtained at a high flow rate due to the increased sample throughput, the quantitative enrichment factor of the VOC did not increase: at the higher flow rate the increased transport of both the VOCs and N_2 across the membrane caused the concentration of the VOCs to not increase in the canister. The experimental data suggest that a sample flow rate of 15 ml/min (linear velocity: 340 cm/sec.) is an optimal parameter for this sampling system at the experimental condition.

At a very low flow rate, both the low enrichment factor and the response observed in Figure 4.6 and 4.7 may indicate the formation of a boundary layers adjacent to the membrane surface. At the low flow rate, poor mixing usually will cause formation of a layer of analyte depletion at the sample/membrane interface which is commonly found when using a flat membrane or aqueous sample[Hariand, et al. (1987); LaPack, (1990); and Shoemaker, (1993)]. The boundary layer impedes the transport of the analytes through the membrane. Therefore a higher flow rate is needed to minimize the possibility of the formation of a boundary layer, which is particularly important for water samples because the rate of diffusion through water for some VOCs may be slower than through the membrane.

The Reynolds number N_{Re} , a measure of the degree of turbulence, is used to calculate the type of flow.

$$N_{Re} = \frac{d_i v \rho}{\mu} \tag{4.18}$$

where d_i is the inner diameter of a tube, v is the sample linear velocity, ρ is the sample density, and μ is the sample viscosity. The transition from laminar flow to turbulent flow occurs at Reynolds number values above 2100 [Geankoplis, (1978)]. To achieve these values, air sample flow rates over 500 ml/min (linear velocity about 10500 cm/sec.) and water sample over 25 ml/min (linear velocity about 570 cm/sec.) at 30 ^{0}C are required for a 0.305 mm I.D. hollow fiber used in this study. At such a high flow rate, however, excess air pressure will cause leakage at the membranes and stainless steel junctions, and may also damage the membranes. Fortunately, for an analytic application, turbulent flow is not necessary for a membrane permeation process. LaPack and co-workers [LaPack, et al. (1990)] studied the effect of the flow rate upon the boundary layer for water samples. They used the change in the permeation rate with the change in the flow rate as a measure of the size of the boundary layer. They found that at a flow rate of approximately 10 ml/min. the boundary layer was insignificant for most volatile organic analytes studied; the changes in response times also becomes small as the flow rates approach 10 ml/min. In another application, 2.5 to 4.0 ml/min were the preferred water sample flow rate [Shoemaker, et al. (1993)].

Since turbulent flow is not necessary for water where high adhesion forces between the molecules exists, it is definitely not necessary for air also where the adhesion forces between the molecules are much weaker, making the formation of a boundary layer less likely. So for air sample, even at relatively low flow rates, high permeation rate is possible. This behavior can be explained by the Schmidt number N_{Sc} which is the ratio of the shear component for diffusivity $\frac{\mu}{\rho}$ to the diffusivity for mass transfer D_{AB}. This dimensionless number physically relates the relative thickness of the hydrodynamic layer and mass-transfer boundary layer.

$$N_{Sc} = \frac{\mu}{\rho D_{AB}} \qquad (4.19)$$

The viscosity and density used are the actual flowing mixture of solute A and fluid B. If the mixture is dilute, properties of pure fluid B can be used. For liquids which have small values of D_{AB}, the N_{Sc} is above 100 and for gases in the range 0.5 - 3 due to high values of D_{AB} [Geankoplis, (1978)]. The low value of N_{Sc} indicates that the air sample has a much thinner boundary layer than the water sample at the same value of N_{Re}. Therefore, the boundary layer can be minimized at relatively lower N_{Re} for air samples which agrees with the experiment data. Throughout the remainder of this study, 15 ml/min to 20 ml/min (linear velocity: 340 - 450 cm/sec.) were the preferred sample flow rates, unless otherwise specified.

4.3.2.3 Effect of Temperature: Since the temperature of the sample flowing over the membrane impacts the permeation rate of VOCs and air, the value of the enrichment factor will be affected. The investigation of the effect of temperature was carried out at temperatures of 0^0, 25^0, and 65 ^{0}C, respectively, by sampling a gas mixture containing 250 ppbv Acetone, 80 ppbv Benzene, Toluene, and Hexane in air. The temperature effects on the enrichment factor are presented in Figure 4.8 and Table 4.5. Experimental results showed that when the temperature increased from 0 ^{0}C to 65 ^{0}C, the enrichment factor decreased 28%, 53%, 54%, and 58% for acetone, benzene, toluene, and hexane, respectively. However, the permeation rate of those volatile compounds will increase with increasing the temperature.

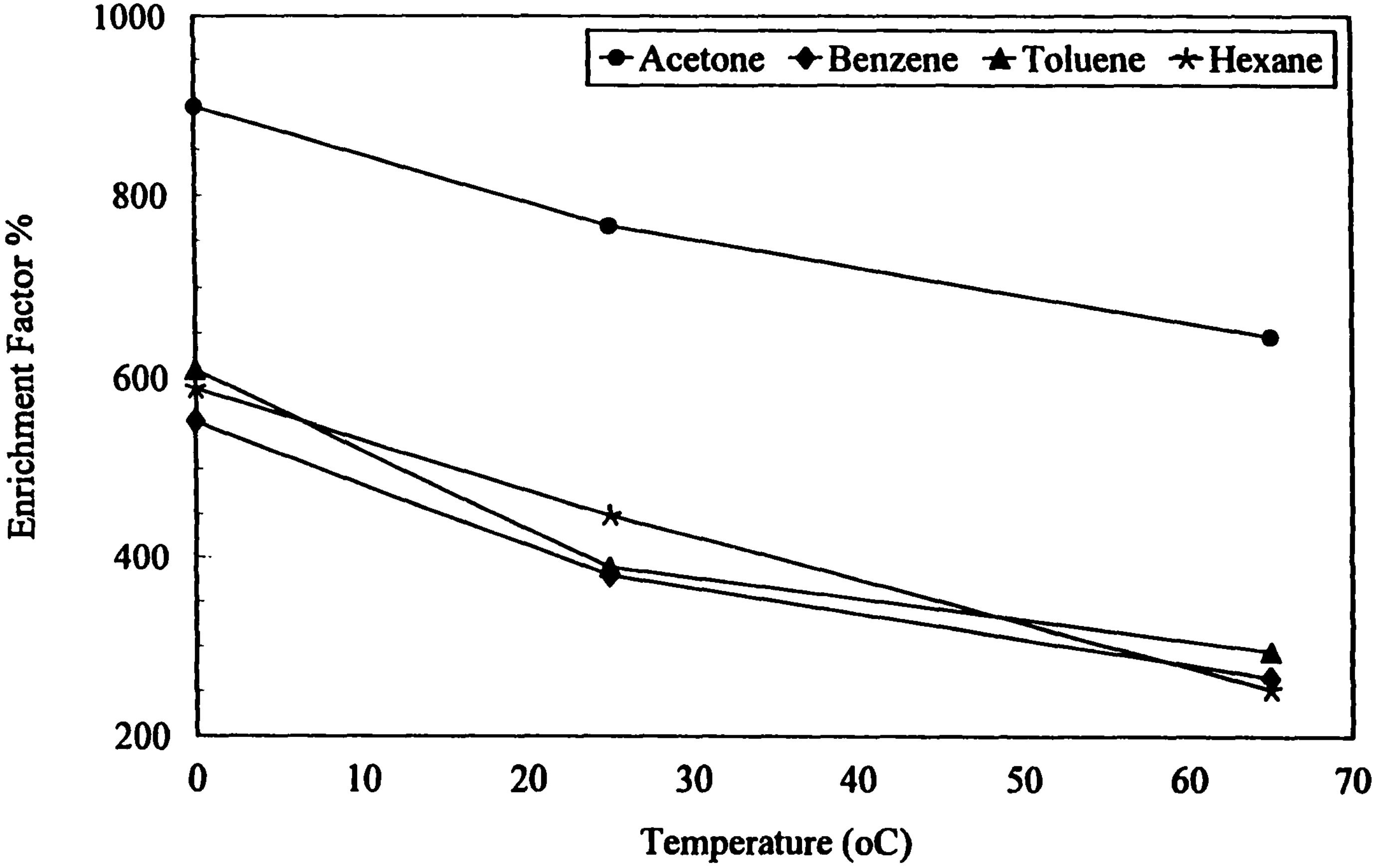


Figure 4.8 The effect of temperature on the enrichment factor. The flow rate was 30 ml/min and pressure was 35 psi.

Table 4.5 The effects of the membrane module temperature on enrichment factor of VOCs

Compound	Acetone	Benzene	Toluene	Hexane
Enrichment Factor% (at 0 ^{0}C)	900	550	650	590
Enrichment Factor% (at 25 ^{0}C)	770	380	390	450
Enrichment Factor% (at 65 ^{0}C)	650	260	300	250

The activate diffusion involved in membrane permeation is dependent upon temperature. Before a species permeates through a non-porous polymeric membrane, it first comes to rest at equilibrium on the membrane surface. If it is activated, i.e. if sufficient extra energy is supplied to that region then the molecule may begin to migrate. The energy is used to open holes (separate polymer segments) through which the permeating species can pass and is to supply kinetic energy for the motion of the molecules. Because this is an "activated" process, it is temperature-dependent and follows the Arrhenius type equations [Kline, (1966); Simril and Hershberger, (1950); LaPack, et al. (1990)]:

$$P = P_0 \exp\left[-E_p\left(\frac{1}{RT} - \frac{1}{RT_0}\right)\right] \tag{4.20}$$

$$D = D_0 \exp\left[-E_d\left(\frac{1}{RT} - \frac{1}{RT_0}\right)\right] \tag{4.21}$$

$$S = S_0 \exp\left[-\Delta H\left(\frac{1}{RT} - \frac{1}{RT_0}\right)\right] \tag{4.22}$$

where the initial permeability P_0, the initial diffusivity D_0, and the initial solubility S_0 are given at a temperature, T_0. The activation energy for the over-all permeation process, E_p, is the sum of E_d, the activation energy for the diffusion process, and ΔH_s, the heat needed to dissolve the permeant in the membrane. Since the permeability P of mass transfer occurring by activated diffusion is the product of the diffusion coefficient D and the solubility coefficient S, the equation 4.20, 4.21 and 4.22 can be rearranged as follows:

$$P = DS = D_0 S_0 \exp\left[-(E_d + \Delta H_s)\left(\frac{1}{RT} - \frac{1}{RT_0}\right)\right] \qquad (4.23)$$

The temperature affects the D and S terms in the equation 4.23 differently because the activation energy E_d is greater than zero, while ΔH_s is less than zero for most VOCs. Consequently with decreasing temperature solubility increases but diffusion decreases. However, the direction for the change in the over-all permeability with changing temperature is dependent upon whether diffusion or solubility is the dominant factor, as determined by the relative magnitudes of E_d and ΔH_s. For air components such as N_2, O_2, diffusion is the predominant mechanism of permeation and decreases with decreasing temperature. However, for organic compounds solubility in membrane plays a critical role. It is the dominating factor and as temperature increases, the solubility decreases. Thus one can expect that as temperature is decreased, more organic compounds will permeate through the membrane with respect to air molecules. As a result, the enrichment factors of VOCs are expected to increase as temperature decrease. In Figure 4.8, it is seen that as temperature was increased, the enrichment factors decreased for all the compounds studied. However, it should be kept in mind that increasing the temperature accelerates the permeation process for VOCs. Enrichment factors could be further increased by lowering the temperature. The results here are in line with reported results. Baker and co-workers reported that the selectivity for Halon 1301 with respect to nitrogen is 2 to 3 at room temperature but increases to the range 10 to 30 when the sample is cooled from -20^0 to -40 ^{0}C [Baker and Wijmans, (1994)].

Efforts were made to enhance enrichment factor by cycling the temperature of the membrane permeator. At low temperatures the solubility of VOCs is increased but at high temperature diffusion is increased. The idea was to first cool the permeator to enhance dissolution of the organic, then the membrane was heated to move the molecules partitioned in the membrane. The cycle consisted of first holding the membrane module at 0 ^{0}C for 30 minutes, then heating to 45 ^{0}C for approximate five minutes. This cycle was repeated during the whole sampling process. Here the membrane almost behaved like an adsorbent. First it is used to trap the organics and then the organic compounds are thermally desorbed. The results of the temperature cycling experiment are compared with continuous permeation at 0 ^{0}C and presented in Figure 4.9. It is seen that enrichment factor increased from 500 to 563 when the temperature was cycled.

4.3.2.4 Effect of the Pressure Differential: The driving force for membrane permeation is the presence of a partial pressure differential. This driving force causes the permeant to flow from high partial pressure (or high concentration) side of the membrane to its low partial pressure (or low concentration) side. Here the pressure on the feed side of the membrane was increased to see what effect it had on the enrichment factor. Since permeation and selectivity are function of temperature as well, the experiment was repeated at 0^0, 25^0, and 65 ^{0}C.

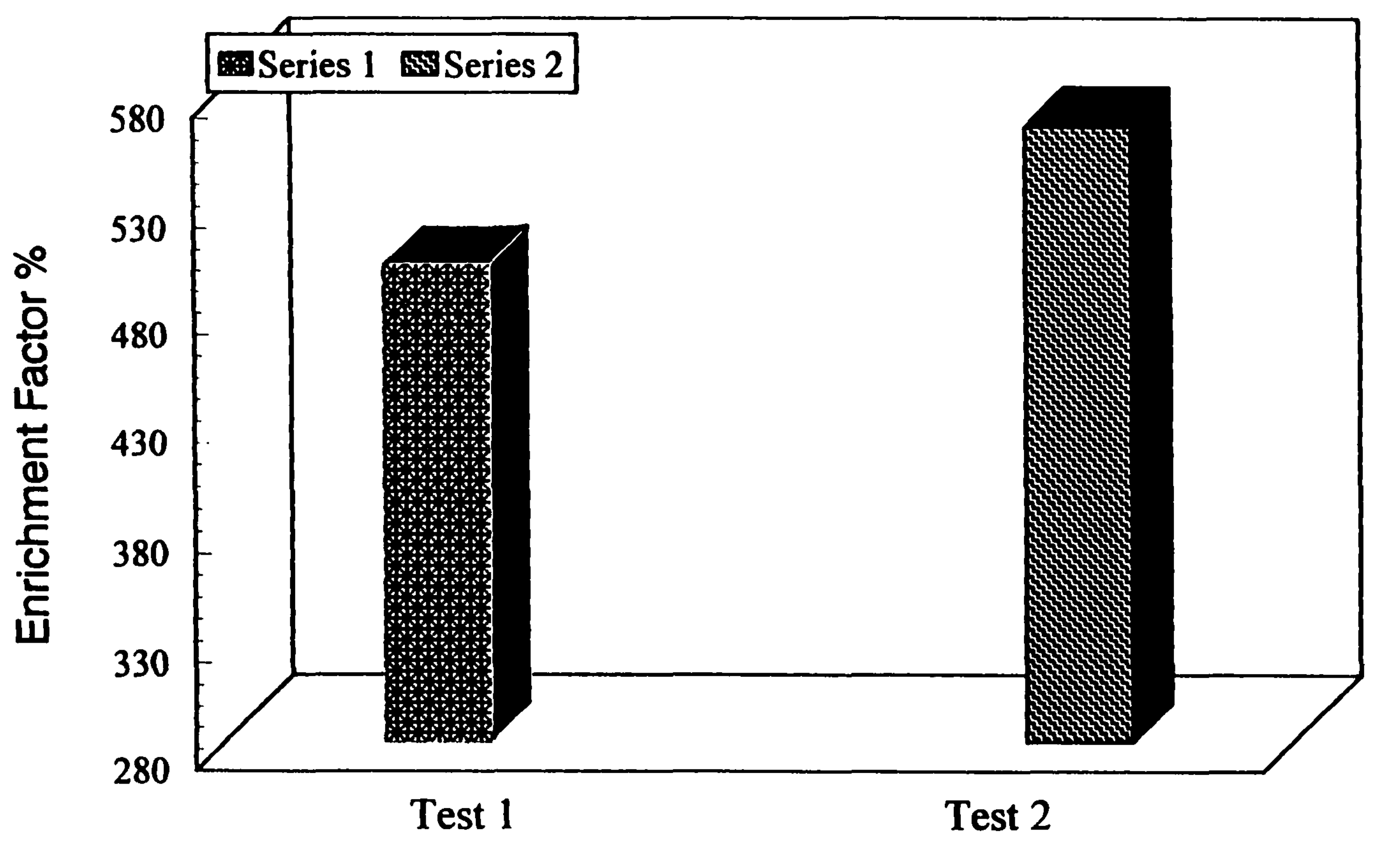
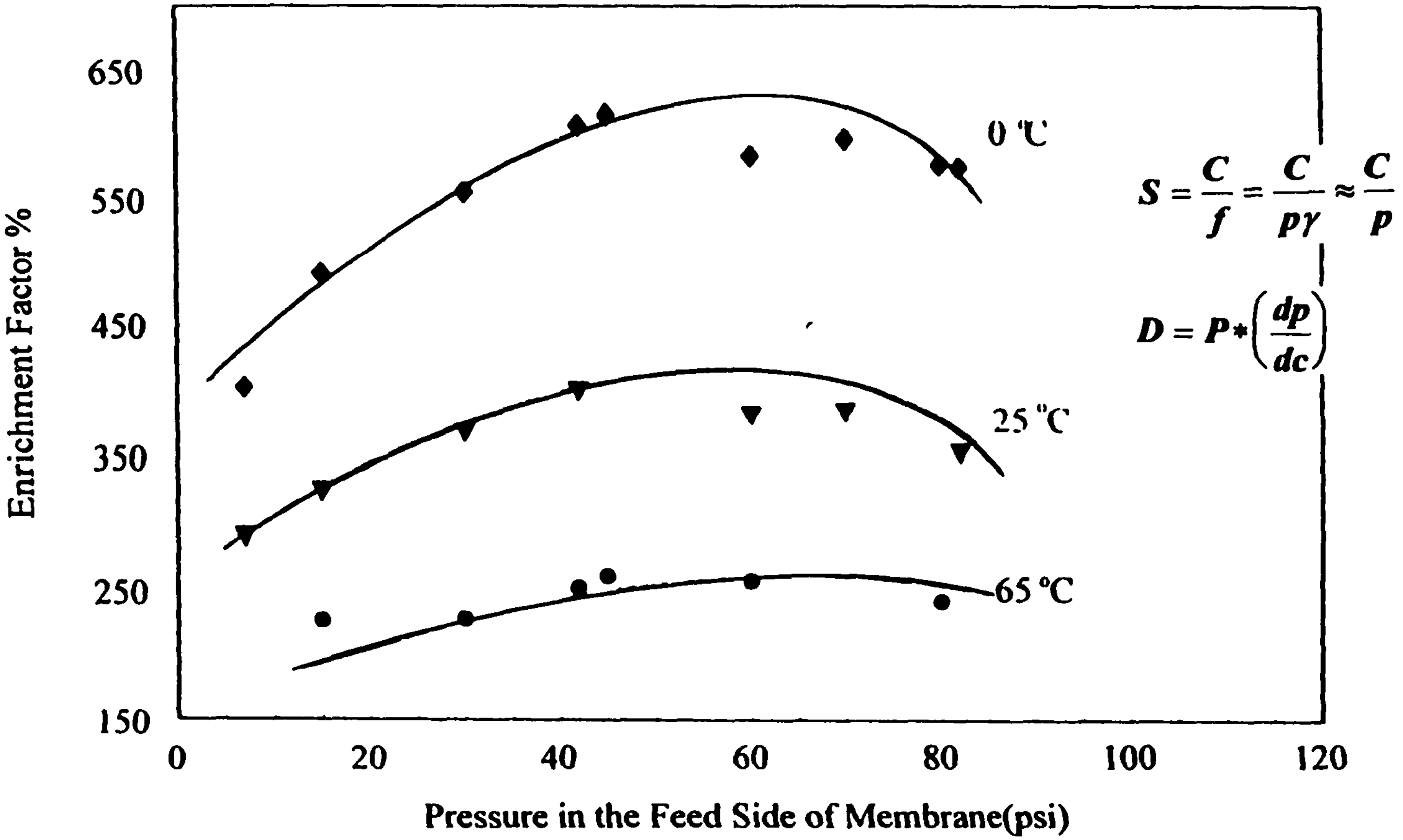


Figure 4.9 Influence of the membrane module temperature on the enrichment factor. Test 1 was carried out under 0 0C and Test 2 was temperatue cycling study. Tested VOC was 200 ppbv toluene in air. Experiment was carried out at flow rate 20 ml/min and feed pressure 32 psi.

The experimental results are presented in Figure 4.10. and illustrate that when increasing the pressure in the feed side of the membrane from 10 psi to 80 psi, the enrichment of Toluene was increased. However, the effect of pressure on the permeation of VOC was different at different temperature and the magnitude of the enrichment increase was larger at lower temperature (0 ^{0}C) than at higher temperature. Another observation from the experiment is that at lower temperature, the enrichment of Toluene increased with increasing the pressure until to a maximum point was reached. Beyond this, enrichment factor began to decrease when pressure was increased. The maxima was not pronounced at 65 ^{0}C.

From the equation 4.1, it is seen that the permeation flux of the VOC across the membrane is directly proportion to the partial pressure gradient of the VOC. Increasing the total pressure in the feed side of the membrane increases the partial pressure gradient for both VOC and the air matrix. However, the effect of pressure difference will vary depending on the nature of the membrane material and the chemical and the physical properties of a permeant. The selectivity of rubbery polymer membrane is usually dominated by differences in solubility between the organic compounds and the air. The solubility of organic molecules in the rubbery membrane commonly increases with increase in pressure. The solubility coefficient, S [cm^3(STP)/(cm^3 cmHg) which indicates how much permeant can be taken up by the membrane when equilibrated with a given gas fugacity f (or pressure p), can be expressed as follows:

$$S = \frac{C}{f} = \frac{C}{p\gamma} \approx \frac{C}{p} \qquad (4.24)$$



$$S = \frac{C}{f} = \frac{C}{p\gamma} \approx \frac{C}{p}$$

$$D = P * \left(\frac{dp}{dc} \right)$$

Figure 4.10 The effect of feed side pressure on the enrichment factor at different temperatures. The test VOC was 1 ppmv Toluene.

The solution-diffusion model assumes that when a pressure is applied across a dense membrane, the pressure every where within the membrane is constant at the high-pressure value. This assumes, in effect, that solution-diffusion membranes transmit pressure in same way as liquid. Therefore, Henry's law can be applied here at low concentration, i.e., solubility coefficient, S, is equal to Henry's constant and independent of concentration C or pressure p. Thus the concentration of VOC in the membrane is proportional to the pressure and will increase with increasing the pressure p.

Furthermore, from the macroscopic irreversible thermodynamic point view, the dissolved permeant molecules in the membrane will move at velocity μ_x by a chemical potential gradient of the permeant in the membrane, $\frac{\partial\mu}{\partial x}$, against the membrane resistance F. Combining the equation 4.23 with the chemical potential expression:

$$\mu = \mu^0 + RT\ln f \approx \mu^0 + RT\ln p \tag{4.25}$$

and defining D_T as the "thermodynamic" diffusion coefficient and equating to RT/F, the amount of permeant moving across a unit cross-sectional area per unit time at a position x is obtained by follows [Petropoulos (1994)]:

$$J = \mu_x C = -\frac{C}{F}\frac{\partial\mu}{\partial x} = -D_T S\frac{\partial f}{\partial x} = -P\frac{\partial f}{\partial x} \approx -P\frac{\partial p}{\partial x} \tag{4.26}$$

Comparing this equation to Fick's law:

$$J_x = -D\left(\frac{\partial C}{\partial x}\right) \tag{4.27}$$

the definition of diffusion coefficient D is obtained as follows:

$$-D\left(\frac{\partial C}{\partial x}\right) = -P\left(\frac{\partial f}{\partial x}\right) \tag{4.28}$$

$$D = P\left(\frac{dp}{dc}\right) \tag{4.29}$$

From this diffusion coefficient equation, it is also shown that concentration of VOC in the membrane increases proportionally with increasing the pressure since permeability P and diffusion coefficient D is constant at low concentration.

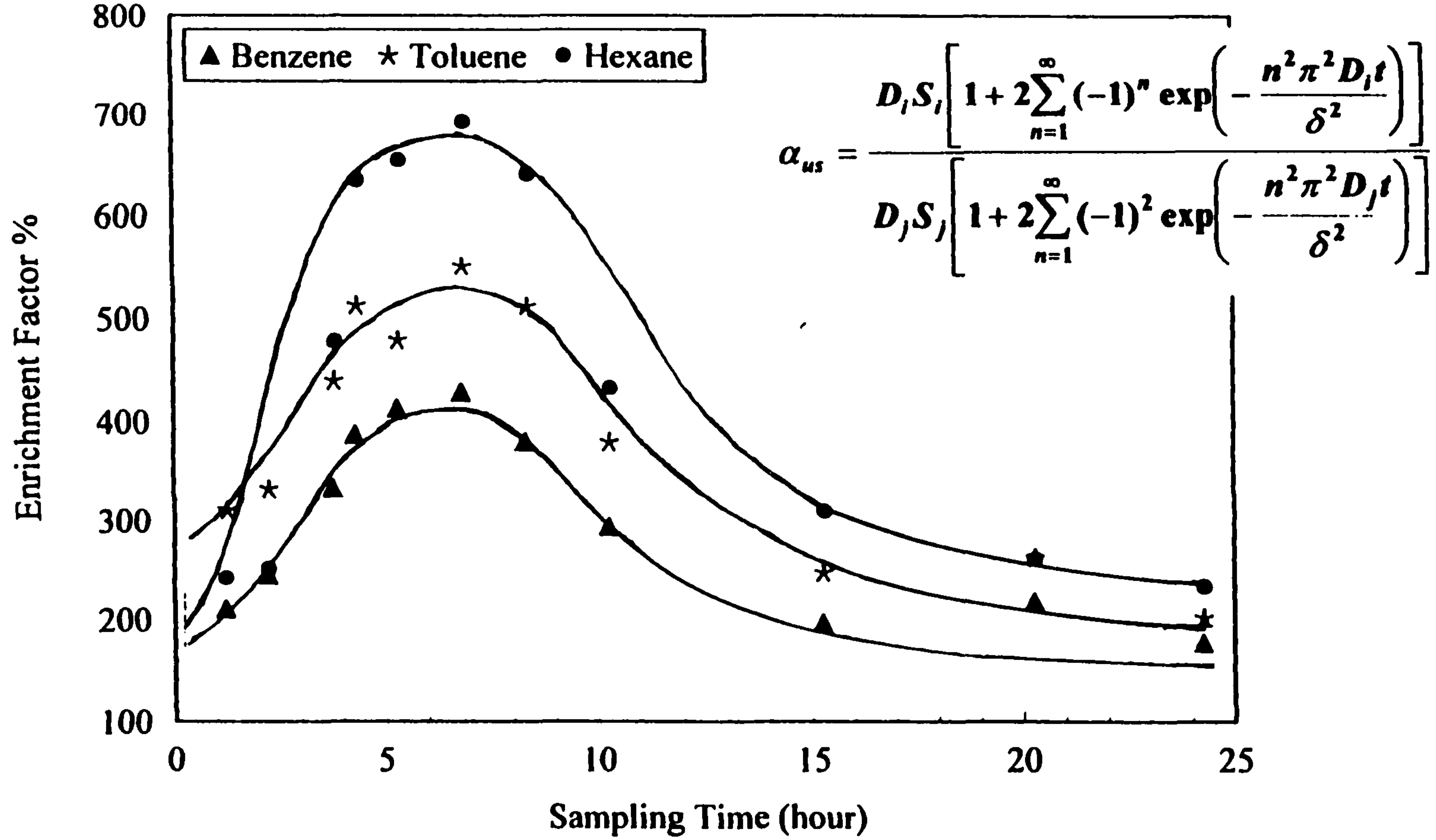
It is noted that although the permeation of the permeant across the membrane will increase with increasing the feed pressure, a limit may exist (Figure 4.10). Past this maximum point, further increasing the feed side pressure caused enrichment of VOC to decrease due to the larger output of air matrix by higher pressure force.

From Figure 4.10, it is also observed that the effect of pressure on enrichment of VOC was larger at low temperature than at high temperature which is consistent with other investigation [Baker and Wijmans, (1994 and 1995)]. Baker and Wijmans reported that cooling the experimental system from 22 to -39 ^{0}C at constant feed partial pressure about 5 psi, the selectivity of Halon 1301, CF3Br, over nitrogen increased from approximate by 4 to 15. However, when the experiment was repeated at the pressure 30 psi, the selectivity increased to almost 28. This phenomena can be partially explained by molecular collision theory [Atkins, (1994)]. The collision number, which is closely related to the permeation of a VOC, is proportional to the temperature as well as the pressure on the membrane surface. At a relative higher temperature, the collision number of VOC may reach a maximum, therefore increasing pressure will not help for further increasing the enrichment of VOC. The collision number of VOC molecules, however, is not at its maximum at lower temperatures and can be further increased by increasing pressure on the surface of membrane, which leads to increase the permeation of a VOC across the membrane. Since both temperature and pressure have complex effect on a permeation process, choosing optimum values for these parameters has to be done carefully depending upon the purpose of the investigation and the experimental conditions.

4.3.2.5 Effect of Sampling Time (Influence of Downstream Pressure): Duration over which the sample is to be collected is an important parameter for canister sampling using the membrane permeator. As the air is sampled, pressure builds up inside the canister, and reduces the partial pressure differential, and thus the driving force for the membrane permeation.

The study on the effect of sampling time on enrichment of VOC was carried out by varying sampling time from a half hour to 24 hours while air was sampled through a single fiber module at constant temperature, feed pressure, and sample flow rate. The experimental results are presented in Figure 4.11 which shows the plots of enrichment factor versus sample collection time for benzene, toluene, and hexane. The inlet concentration was 300 ppmv. For sample collection time less than about 2-3 hours, the enrichment factor for all the compounds increased steadily with increasing sampling time. Then, the enrichment of VOC reached a maximum range where it stayed constant for approximately 3-4 hours. However, after sampling time above about 7-9 hours, the enrichment of VOC declined with increasing sample collection time. Beyond approximately fifteen hours, the enrichment factors of VOCs showed no change at all.

It should be kept in mind that as sampling time increases, the pressure in the canister increases and the relationship is shown in Figure 4.12.



$$\alpha_{us} = \frac{D_i S_i \left[1 + 2\sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2 \pi^2 D_i t}{\delta^2} \right) \right]}{D_j S_j \left[1 + 2\sum_{n=1}^{\infty} (-1)^2 \exp\left(-\frac{n^2 \pi^2 D_j t}{\delta^2} \right) \right]}$$

Figure 4.11 The effect of sampling time on the enrichment factor. A single fiber module was used.

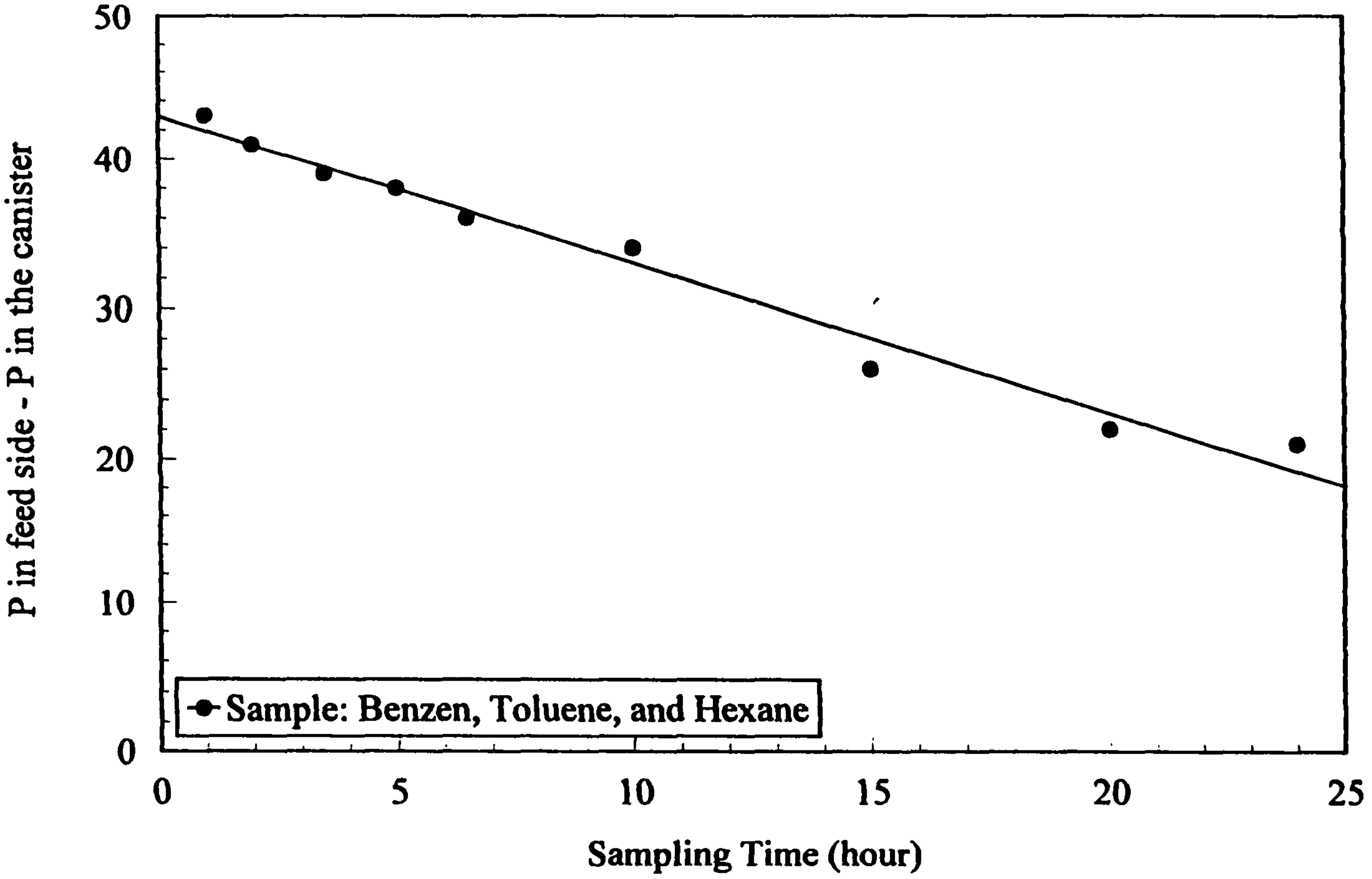


Figure 4.12 The relationship between system pressure differential and sampling time.

It was expected that the enrichment factor would be maximum at low sampling time as the canister pressure is very low, providing a high partial pressure gradient for permeation. However, the results in Figure 4.11 did not demonstrate that. Two possible reasons were: a) membrane permeation process is very slow and analytes have not completely permeated into the canister; b) the active sites on the canister surface have to saturated before the concentration builds up in the canister. In our previous publication [Mitra, et al. (1996)] we reported that for gases the permeation time is only about 30 sec. to 2 minutes. Thus, the later is the more viable reason that the enrichment factor continued to rise for the first 2-3 hours. Since the concentration of VOC in the feed stream was small, the amount of VOC permeated was also small in the beginning, and much of it was strongly adsorbed on the canister surface. Compared to larger VOC molecules, nitrogen doesn't absorb on the canister surface easily because its Van der Waal's forces are extremely weak as evidenced by its extremely low boiling point.

Along with increasing sample collection time the pressure in the canister increases and downstream pressure on the permeate side of the membrane will build up which decreases the driving force for VOC transport. However, the experimental results illustrate that the enrichment of VOCs could remain approximately constant for four hours at the experimental condition, which indicated that at low downstream pressure range, the permeation rate of VOC was relatively insensitive to the downstream pressure due to a slight decrease of the driving force for VOC permeation. These results agree with other investigators [Ji et al. (1994)].

Further increasing the downstream pressure resulted in a rapid decrease of the enrichment of VOC demonstrated by the last portion of the plot in Figure 4.11 due to the significant decrease of the driving force for VOC permeation. Moreover, the effect of the nitrogen back pressure played a important role in this permeation process. While the rate of diffusion of nitrogen into the canister remained steady with time, its concentration would increase in the canister because it acted as an accumulator: this is evidenced by the steady increase in pressure with time in the canister (Figure 4.12). But the concentration of VOC molecules decreased with increasing pressure. The VOC molecules have to become detached from the membrane to get into the canister stage. This is an endothermic process but favored by the increase in entropy as the VOC molecules become more randomly dispersed. From kinetic theory, it is evident the nitrogen molecules diffuse back from the canister stage into the membrane. That backward diffusion will cause collisions between the relatively few exiting VOC molecules and the returning nitrogen molecules. Since the backward diffusion rate of the nitrogen molecules increases with the back pressure, a pressure is reached such that the collisions caused by the returning nitrogen molecules causes the rate of detachment of the VOC molecules to drop. This is attributed to that the transfer of momentum from the collisions causes an ever increasing number of VOC molecules to be driven back into the membrane. In other words, the driving force for detachment, the increase in entropy associated with disorder, is overcome by the force due to the transfer of momentum during the collisions.

Therefore, when the downstream pressure has the effect on the permeation rate, the system is in a unsteady-state condition and time interval of sampling is considerable important. Time interval influence on enrichment of VOC can also be observed obviously from the expression of a unsteady-state separation factor, α_{us}:

$$\alpha_{us} = \frac{D_i S_i \left[1 + 2\sum_{n=1}^{\infty} (-1)^n \exp\left(-\frac{n^2 \pi^2 D_i t}{\delta^2} \right) \right]}{D_j S_j \left[1 + 2\sum_{n=1}^{\infty} (-1)^2 \exp\left(-\frac{n^2 \pi^2 D_j t}{\delta^2} \right) \right]} \qquad (4.30)$$

From this equation, it can see that at short diffusion times larger separation factors are reached, and, when $t \to \infty, \alpha_{us} \to \alpha_{ss}$. Thus, the time interval of sampling which provides a maximum enrichment of VOC should be selected.

Quantitative calculation of the permeation rate of a VOC across the membrane can be achieved using a kinetic mathematic modeling which is going to be discussed in the following chapter.

4.4 Summary

This study has demonstrated that membrane permeation is an excellent technique for sampling non-polar as well as polar volatile organic compounds into a whole air sampler such as a canister. The vacuum in the canister provides the partial pressure gradient required for sample preconcentration. Using this new sampling device, as much as few fold enrichment of VOC was obtained compared to direct collection using a canister alone. Another advantage of the MPCS system is that it eliminates water from the air sample and thus acts as a water management device. Furthermore, the study also shows that this system can be used to study the permeation mechanism of VOCs at trace concentrations and can provide data to refine the theoretical models needed to propel the more sophisticated membrane applications at trace levels.

CHAPTER 5

SELECTIVE CONCENTRATION OF VOCs INTO A CANISTER BY A MEMBRANE PERMEATOR
(PART II: CHARACTERISTICS AND APPLICATION)

5.1 Introduction

In the previous chapter, a membrane permeator was presented for canister sampling of VOCs in air. The study demonstrated that membrane extraction can be utilized to selectively concentrate the organic compounds from air into a canister. This increases the sensitivity of the canister analysis and lowers the detection limit. This technique referred to as Membrane Permeation Canister Sampling (MPCS) was also used to study the kinetic and thermodynamic aspects of permeation of the trace level volatile organic compounds through membranes. There is considerable amount of data in the literature concerning permeation of permanent gases through polymer membranes and much less data on the permeation of organic compounds especially at trace levels. Therefore, the factors that affect organic permeation are not well understood. The further investigation carried out in this research focuses on understanding the characteristics of the membrane permeator and its applications as an air sampling device.

Permeation is a function of the properties of both the polymeric membrane and the permeant. Usually the permeation rate increases with decreasing size of the permeant molecule and with increasing ease of condensation. Enhanced permeation occurs when the permeant and the membrane material have similar chemical properties [Houde, et al. (1995); Patil, et al. (1995)]. In this study, the relationship between membrane structure (material and thickness) and VOCs enrichment has be investigated. The Kinetics of membrane extraction has also be discussed and a mathematical model developed to determine a suitable sampling time to achieve a high enrichment of VOCs. Another objective of this study is to evaluate this new sampling device by collecting real ambient air sample at three different places.

The analytical system used for air analysis is shown in Figure 5.1. Instead of conventional cryogenic traps, a microtrap was used to concentrate and inject analytes into a GC column. A microtrap is a small diameter tubing packed with one or more adsorbents. The details of microtrap characteristics have been presented elsewhere [Mitra and Lai, (1995); Mitra and Chen, (1995); Mitra, et. al. (1996)]. In this study, a multibed microtrap, containing mainly Carbotrap™ C and small portion of Carbopack™ B and Carbosieve™ S-III, was used to replace the sample loop of a six-port valve which connected to a GC and a vacuum system. During the sampling mode, the vacuum pump pulled the air sample from a canister through the microtrap, in which VOCs were selectively trapped. And then the valve was switched to the injection mode: the microtrap was electrically heated to inject the analytes into the GC. The desorption was carried out in a backflush mode (Figure 5.2). The main advantage of backflush desorption is high desorption efficiency for compounds which are difficult to desorb.

5.2 Experimental Section

The study was done with standard air sample containing ppbv level toluene or with a standard containing ppbv level acetone, benzene, toluene, and hexane. The sample stream was 40 psi and passed through the membrane permeator ("flow-through" configuration)

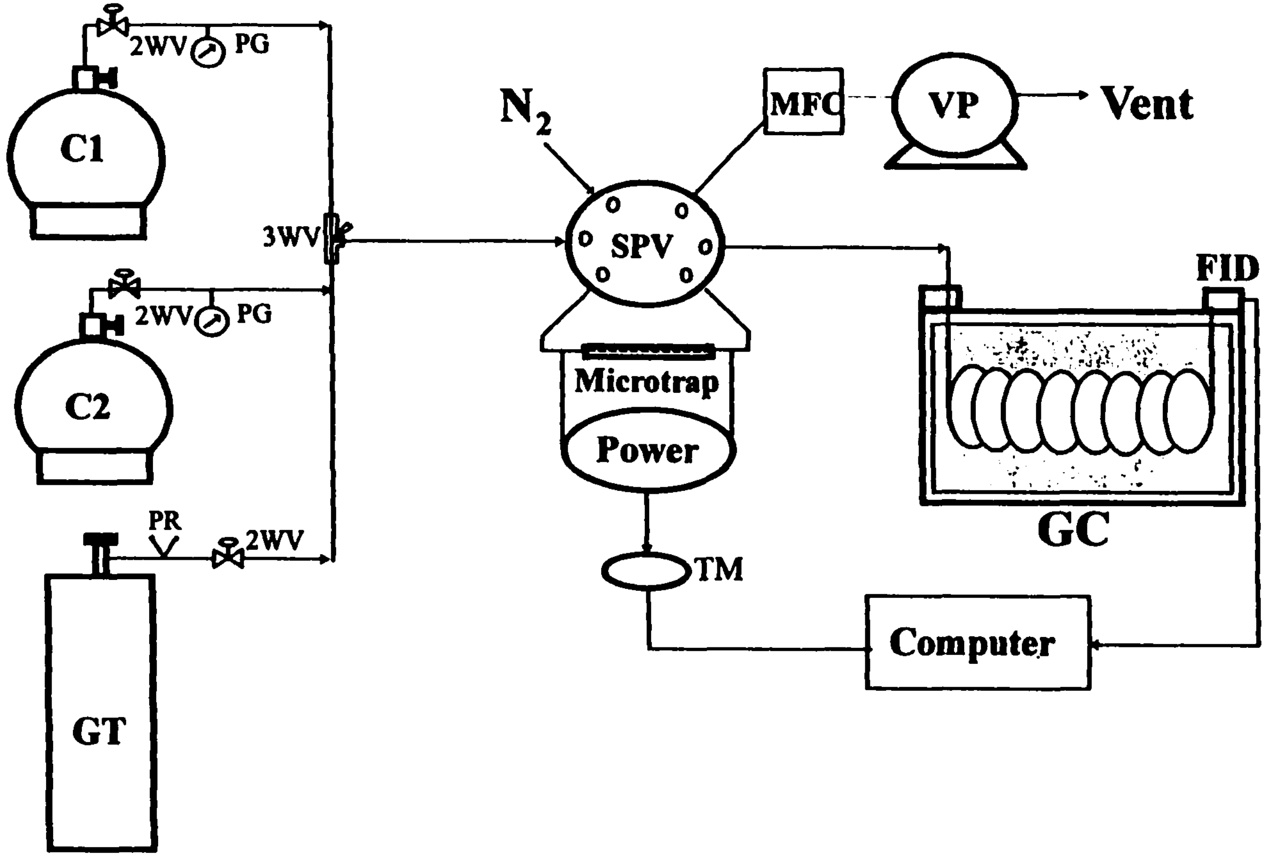


Figure 5.1 Schematic diagram of the VMMGC analytica system. C1: Canister for samples; C2: Canister for standards; GT: Nitrogen gas tank; 2--WV: 2-way valve; 3-WV: 3-way valve; PG: pressure gauge; PR: pressure regulator; SPV: six-port valve; MFC: mass flow controler; VP: vacuum pump; TM: timer.

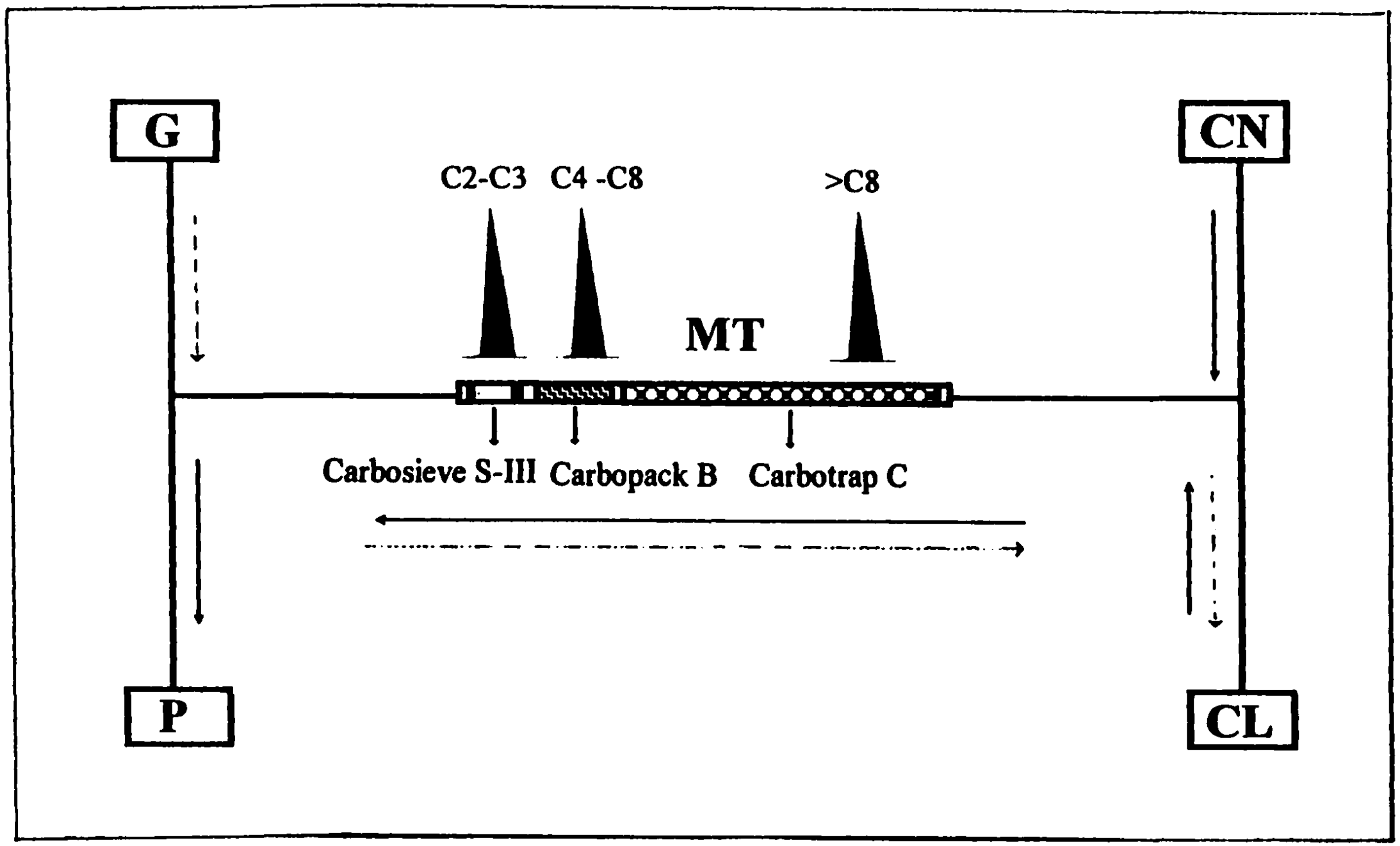


Figure 5.2 The concept of the backflush sample collection system: G: carrier gas supply; P: vacuum pump; CN: canister; CL: capillary separation column; MT: microtrap. Solid lines with arrows show flow directions during the sample collection. Broken lines with arrows show flow directions during analysis.

at a flow rate 15 to 20 ml/min. Membranes of different thickness of silicon fibers or Teflon membrane were used.

Real air samples were collected at three different sites. To compare the enrichment effect of the membrane, samples were simultaneously collected using a canister without the membrane permeator. A membrane "bundle" was used such that the air was directly exposed to the membrane. VOCs selectively migrated across the membrane into the evacuated canister until the pressure increased to a certain value. In the most cases, the final pressure reached approximately -10 inchHg. Duplicates were also collected. After sampling, all samples were brought back to the lab for analysis.

An analytical system referred to as valve-multibed-microtrap-GC (VMMGC) for analyzing trace level VOCs in the low pressure canister was designed. The trap was designed to retain VOCs of a wide range of volatility. It contained layers of three different adsorbents. The microtrap was a stainless steel tubing: 1.4 mm I.D. x 1.8 mm O.D. x 15 cm long and packed with 70 mg of 20/40 mesh Carbotrap™ C, 10 mg 60/80 mesh of Carbopack™ B, and 5 mg 60/80 mesh of Carbosieve™ S-III, respectively (Figure 5.2). All adsorbents were supplied by Supelco Company (Bellefonte, PA, USA). Some characteristics of these adsorbents is listed in Table 5.1.

Carbotrap™ C and Carbopack™ B graphitized carbon blacks are ideal adsorbents for trapping a wide range of airborne organic compounds. The coarse particle size (20/40 mesh) chosen for Carbotrap™ C prevents high back pressure and the entire surface of carbotrap adsorbents is available for interactions that depend solely on dispersion (London) forces. The large surface area of Carbosieve S-III makes it excellent for trapping molecules as small as C_2 hydrocarbons. The pure carbon framework permits thermal desorption of the molecules without loss.

Table 5.1 The characteristics of three adsorbents used in the study

Adsorbent	**Carbotrap™ C**	**Carbopack™ B (Carbotrap)**	**Carbosieve™ S-III**
Coarse particle size	20/40 mesh	60/80 mesh	60/80 mesh
Surface area	10 m2/gram	100 m2/gram	820 m2/gram
Structure	graphitized carbon blacks	graphitized carbon blacks	spherical carbon molecular sieve (15/40 angstrom pores)
Application	trap: $>C_8$	trap: C_4-C_8	trap: C_2-C_3
Thermal desorption temperature	$\geq 400\ ^0C$	$\geq 400\ ^0C$	$> 400\ ^0C$

During the analytical process, the sample was first drawn by a vacuum pump from a canister to pass through the multibed microtrap installed in the six-port gas sampling valve at an average flow rate approximately 20 ml/min for 60 minutes. Then, the six-port valve was switched to the injection mode and the system was first purged with nitrogen for two minutes at a flow rate of 20 ml/min. At the injection position, the microtrap was electrically heated (or pulsed) for four second at a current 50 A and trapped VOCs were desorbed into the GC column by rapid heating which served as an injection for GC separation.

A Hewlett Packard gas chromatograph of Model 5890 Series II equipped with a conventional flame ionization detector and a capillary column DB 624 supplied by J & W

Scientific (Folson, CA, USA) was used for separation. The analytical column was 30 m long and 0.25 mm I.D. and 0.32 mm O.D. with a 1.8 μm thickness of the stationary phase. The conventional injection port of the GC was bypassed and the samples were injected directly into the column through the microtrap. The general operating conditions for GC-FID were selected as follows: the flow rate of N_2 carrier gas was 5 to 10 ml/min, air flow was 350 ml/min, hydrogen 30 ml/min, and the make up gas 20 ml/min. The detector temperature was 250 ^{0}C and the whole transfer line kept at 150 ^{0}C which was same as the temperature in the injection port to prevent any condensation of VOCs. The HP Chemstation 3365 software package was used for data acquisition and analysis.

The gas standards were obtained from AIRLIQUIDE Inc. (Morrisville, PA, USA), one of which contained 2 ppmv toluene and 4.8 ppmv acrylonitrile and ethyl acrylate, respectively, and another contained 1 ppmv of benzene, toluene, trichloroethane, and ethylbenzene, respectively. Summa^{TM} canisters were supplied by Scientific Instrumentation Specialists (Moscow, ID) and the vacuum pump was obtained from EMERSON (Model: SA55NXGTE-4870, St. Louis, MO, USA). The digital pressure gauge was TIF9675 and supplied by TIF Instruments, Inc. (Miami, FL, USA).

Two different configurations were used for constructing the membrane modules. The “flow-through” configuration was used for studying the effect of membrane material and thickness on the permeation and enrichment of VOCs. In this experiment two different membrane materials were used: silicon fibers and Teflon type membrane. The two sizes of the silicone membranes used were: 0.305 mm I.D. x 0.635 mm O.D. from Technical Products, Inc. (Decatur, Georgia, USA) and 0.206 mm I.D. x 0.260 mm O.D. composite membrane in which polypropylene support material was coated with 1 μm siloxane film supplied by Applied Membrane Technology, Inc. (Minnetonka, MN, USA). Similar size membrane with Teflon coating was also used (ANIT #206AKS).

The membrane module used to sample ambient air sample is shown in Figure 5.3. The idea here was to expose maximum of membrane surface to air. The sampling was passive and no forced air flow was used. The vacuum in the canister drew the sample into the canister. The membrane permeator contained 40 silicone fibers, each approximately 50 cm long. The membrane used for the real sample collection was Dow Corning Silastic medical-grade tubing: 0.305 mm I.D. x 0.635 mm O.D. (Dow Corning Corporation, Midland, MI, USA).

5.3 Results and Discussion

5.3.1. The Relationship Between Membrane Structural/Permeation/Selectivity

5.3.1.1 Effect of Membrane Material: Various aspects of the membrane material influence the permeation of VOCs. These include its chemical composition, its similarity in polarity to the permeant, the proportion of crystallinity, polymer orientation in the absence of crystallization, the degree of cross-linking, etc.[Dennis and Larson, (1975?); Crank and Park, (1968); Plate, et al. (1990); Fritsch, et al. (1993); Shah, et al. (1995); Stern, (1994)]. Use of the right membrane thus can result in a large increase in mass fraction of VOCs in the permeated matrix. Unfortunately we had access to a limited number of types of membranes and were not able to evaluate the whole spectrum of membrane features.

The membrane materials typically used for separating and concentrating VOCs in aqueous solution or in air are organic polymers, such as polyethylene, Teflon, and

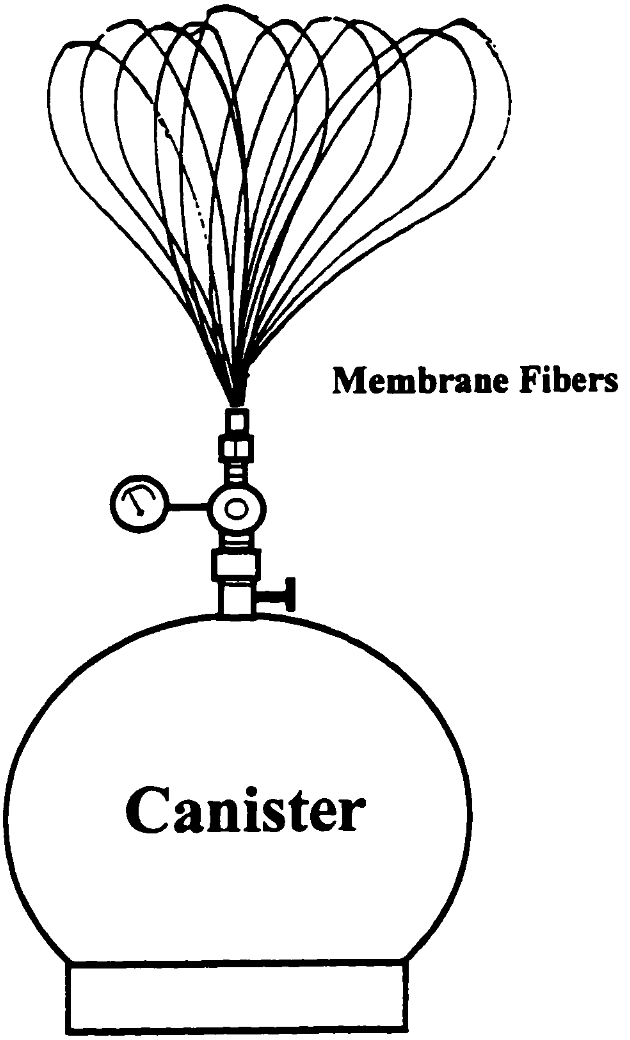


Figure 5.3 The diagram of a MPCS sampling system for ambient air collection.

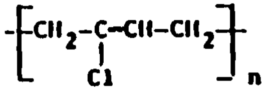
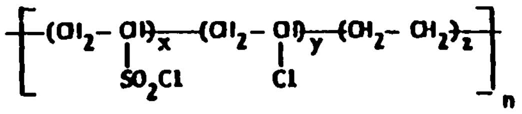
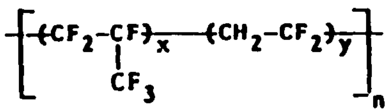
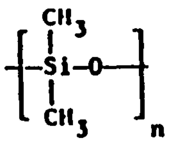
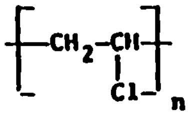
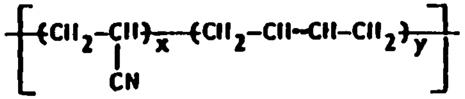
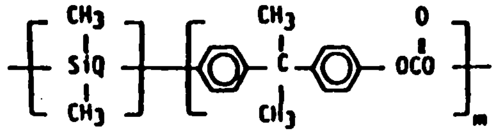
Polymer	Chemical Formula	Supplier	Features
Neoprene, chloroprene	 $\left[CH_2-\underset{Cl}{C}-CH-CH_2\right]_n$	DuPont	
Hypalon® chlorosulfinated polyethylene	 $\left[(CH_2-\underset{SO_2Cl}{CH})_x-(CH_2-\underset{Cl}{CH})_y-(CH_2-CH_2)_z\right]_n$	DuPont	soluble in toluene; several grades available
Fluorel® fluoroelastomer	 $\left[(CF_2-\underset{CF_3}{CF})_x-(CH_2-CF_2)_y\right]_n$	3M	available in a number of grades
Polydimethyl siloxane	 $\left[-\overset{CH_3}{\underset{CH_3}{Si}}-O-\right]_n$	Dow Corning	available as polymerizable oligomers or linear polymers; because of high O_2/N_2 permeability may not be sufficiently permselective
Polyvinyl chloride	 $\left[CH_2-\underset{Cl}{CH}\right]_n$	Goodrich	can be easily plasticized to vary permeability and physical properties
Nitrile rubber, polyacrylonitrile-butadiene	 $\left[(CH_2-\underset{CN}{CH})_x-(CH_2-CH-CH-CH_2)_y\right]$	ChemSamples	available in a number of grades
Silicone poly-carbonate (GE-MEM-213)		General Electric	supplied as 2 mil crosslinked film

Table 5.2 Candidate polymer for organic vapor permeation membrane [Baker].

silicone-based polymers. The chemical structure (chemical formula) for some of those organic polymers are listed in the Table 5.2. Those organic polymer membranes have functional groups or chain segments chemically similar to the permeant, so that the cohesive forces between the polymer and organic species are large, resulting in high solubility of the permeant in the membrane. This increases overall permeability which is a product of the solubility and diffusion coefficient. Moreover, the high concentration of the permeant in the membrane may cause it to swell, resulting in a less "tight" polymer network that will increase the diffusion coefficient which in turn results in a further increase in permeability.

The effects of the membrane material on VOCs enrichments in this study were tested by comparing poly dimethylsiloxane membrane with a Teflon type polymer both of which are composite membranes and have the same supporting material and the same top film thickness. The results of the investigation were presented in Table 5.3 and Figure 5.4.

Table 5.3 The enrichment factors using different membrane material

Compounds	**Hexane**	**Toluene**	**Benzene**	**Acetone**
M#1: Enrichment Factor% (silicone composite membrane)	213	210	143	109
M#2: Enrichment Factor% (Teflon composite membrane)	298	335	250	184

Form the table, it is seen that Teflon type polymer had better selectivities for testing organic species: the enrichment factors were higher than those using silicon rubber.

The greater permeation of the tested VOCs through Teflon, compared to silicone

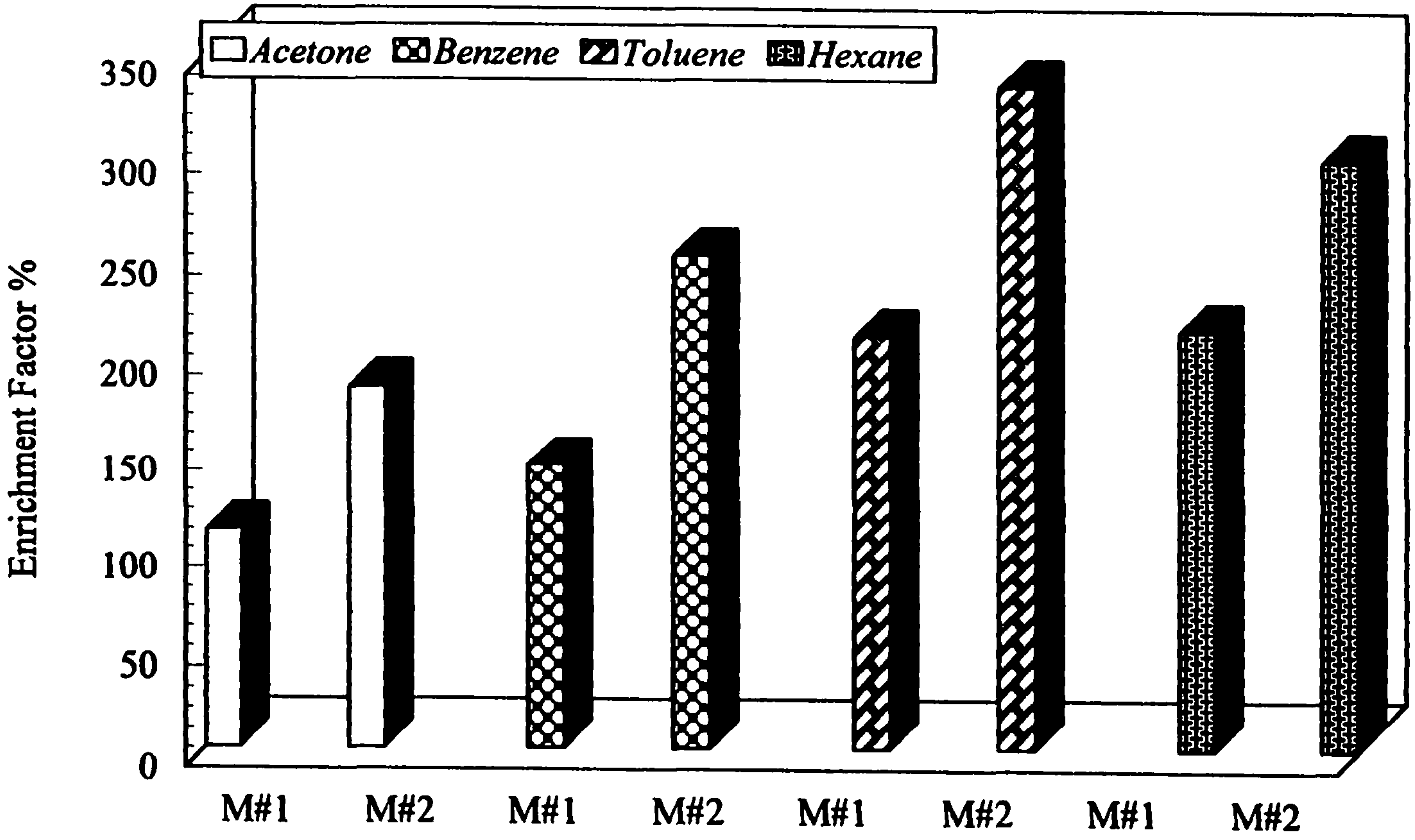


Figure 5.4 Comparison of the effect of the different membrane material on the enrichment of VOCs. M#1: Silicone composite membrane; M#2: Teflon composite mebrane.

membrane, may suggests that Gibb's Free Energy ΔG is more favorable for the solution of the VOC molecules in the Teflon polymer sites. There are two factors which affect the Gibb's Free Energy: the bonding force-enthalpy, ΔH, and the randomness ,entropy, ΔS. The relationship between them can be expressed as follows:

$$\Delta G = \Delta H - T\Delta S \tag{5.1}$$

$\Delta G < 0$, spontaneous

$$\Delta H = \Delta H_{polymer} - \Delta H_{gas\ phase} \tag{5.2}$$

$$\Delta S = \Delta S_{polymer} - \Delta S_{gas\ phase} \tag{5.3}$$

The driving force in both polymers is the enthalpic force because the bonding between the VOC molecules and the polymer favors permeation, while the entropy change that results in more order of the VOCs in polymer than outside the polymer is an unfavorable driving force. However, it is the overall effect that is determinative as expressed in the Gibb's Free Energy which weighs both the enthalpy and the entropy changes. Thus, in order to account for the observed increased permeation of the VOCs in the Teflon polymer over the silicone polymer, both driving forces: the enthalpic and entropy driving forces have to be considered, respectively. Each will considered in turn.

The enthalpic driving force has to be the bonding force between the polymer and the VOC molecules because, outside of the membrane, the VOC intermolecular bonding forces are weak. They are present in the gas state where intermolecular forces are always weak. In the polymer, the bonding forces between the polymer molecules and the VOCs are also weak, but not as weak as in the gas phase. Otherwise, the VOCs would not permeate the membrane. Such weak intermolecular bonding forces have to be Van der

Waal forces. This force, caused by fluctuating dipoles due to the motion of the electrons within the molecules, is proportional to the total number of electrons in the molecules. Since the VOCs are the same in the test for two kinds of membrane, it is the polymeric molecules that bring about the difference. Comparing both polymers, the major difference is the relatively large size of the silicon atom. That means there are more electrons in the silicone polymer, and thus it will exert a greater Van der Waal's force. If the enthalpic force were the determining force, then permeation through the silicone polymer should be greater. But the permeation was found to be less so it is concluded that the enthalpic effect could not be the determining force for the overall permeation process.

The major entropy effect to be expected in this process is the entropy of solution of the VOC molecules into the polymer matrix. Again, the major difference between the two polymers is the silicon atom which is considerably bulkier than the other atoms. That bulk can be expected to cut down on the access of the VOC molecules to the solution sites and the availability of such sites. Relatively speaking, the entropy of mixing will be lower in the silicone polymer than in the Teflon polymer. It appears that the magnitude of the negative entropy change in the silicone polymer is great enough to offset the advantage that the silicone polymer has based upon the enthalpic driving force. In other words, while the enthalpic force is more favorable for the silicone polymers because of the predicted higher Van der Waal's force-this is now then affect by the relatively less negative entropy change in the Teflon polymer because the bulky silicone atom causes more order, less dispersion, in the silicone polymer. Therefore, the overall effect favors permeation through the Teflon polymer.

Although silicone polymer's selectivity is not the highest one, it was used mainly in this study for the following reasons. Firstly, this polymer has shown good permeation rates together with reasonable selectivities, and secondly it has been studied in the past, which allows for comparison of data.

A number of the methods have been proposed for correlating the permeability to different physical properties or structural of polymer membranes and permeants. for example, one of the oldest correlation was proposed by Stannett and Szwarc [Stannett and Szwarc, (1955)]:

$$P_{i,k} = F'(polymer)G'(gas)\gamma'(i,k) \tag{5.4}$$

where F' is a factor which depends on the nature of the membrane, G' is depends on the nature of the gas, γ ' accounts on the interaction between membrane and the gas, and i, k represents the polymer membrane and gas, respectively. The values of F' and G' at 30 ^{0}C have been listed for a several polymer membranes. Thus, it is possible to predict permeabilities for some light gases. Another correlation used often by some investigators was reported by Lee [Lee, (1980)]:

$$P = A\exp\left(-\frac{B}{SFV}\right) \tag{5.5}$$

where A and B are characteristic constants depending upon the properties of both the membrane material and permeant; SFV is the specific free volume. Various of other empirical or semi-empirical correlations of permeability have been proposed in the literatures. Some of them have been discussed and reviewed by Alexander [Alexander, (1994)].

5.3.1.2 Effect of the Membrane Thickness: Choosing a suitable thickness of the membrane is another important consideration for a membrane permeation process. The effect of the membrane thickness on the membrane enrichment was investigated by sampling 200 ppbv toluene in an air sample using a 330 μm thick silicone membranes and a porous polypropylene with 1 μm thick silicone film. The experimental results are presented in Figure 5.5 and Table 5.4.

Table 5.4 Enrichment factor using different membrane thickness

Membrane Thickness	**Thin Film (1 μm)**	**Thick Film (330 μm)**
Enrichment Factor%	311	1274

The experimental results exhibit that the enrichment factor for the thick film was about four times higher than thin one. The investigation results are consistent with other reporters [Baker and Wijmans, (1994)]. Baker and co-workers' study showed that the intrinsic selectivity of silicone rubber for a Tetrachloroethylene/nitrogen system is over 50, but a selectivity of greater than 40 is not achieved until the silicone rubber layer is thicker than 8 μm and the selectivity is less than ten using 1 μm, as shown in Figure 5.6.

Selectivity of VOCs with respect to air was higher for thick membranes than with thin-film composite membrane. This difference is due to the following reasons. The first step in the permeation of the VOC molecules through the membrane involves collision of the VOCs with the surface of the membrane. Since the selectivity of thin membranes is lower than thick one, it follows that the sticky collisions do not occur on the surface

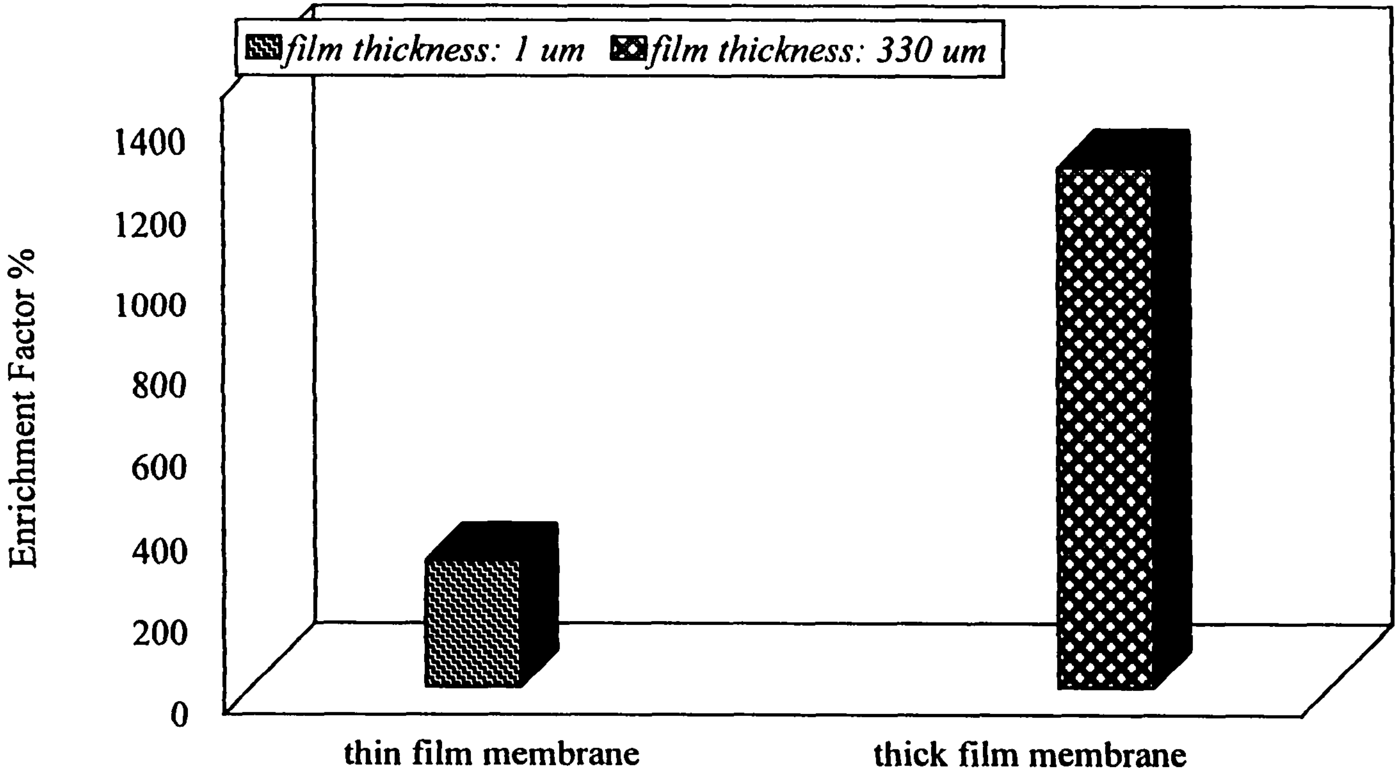
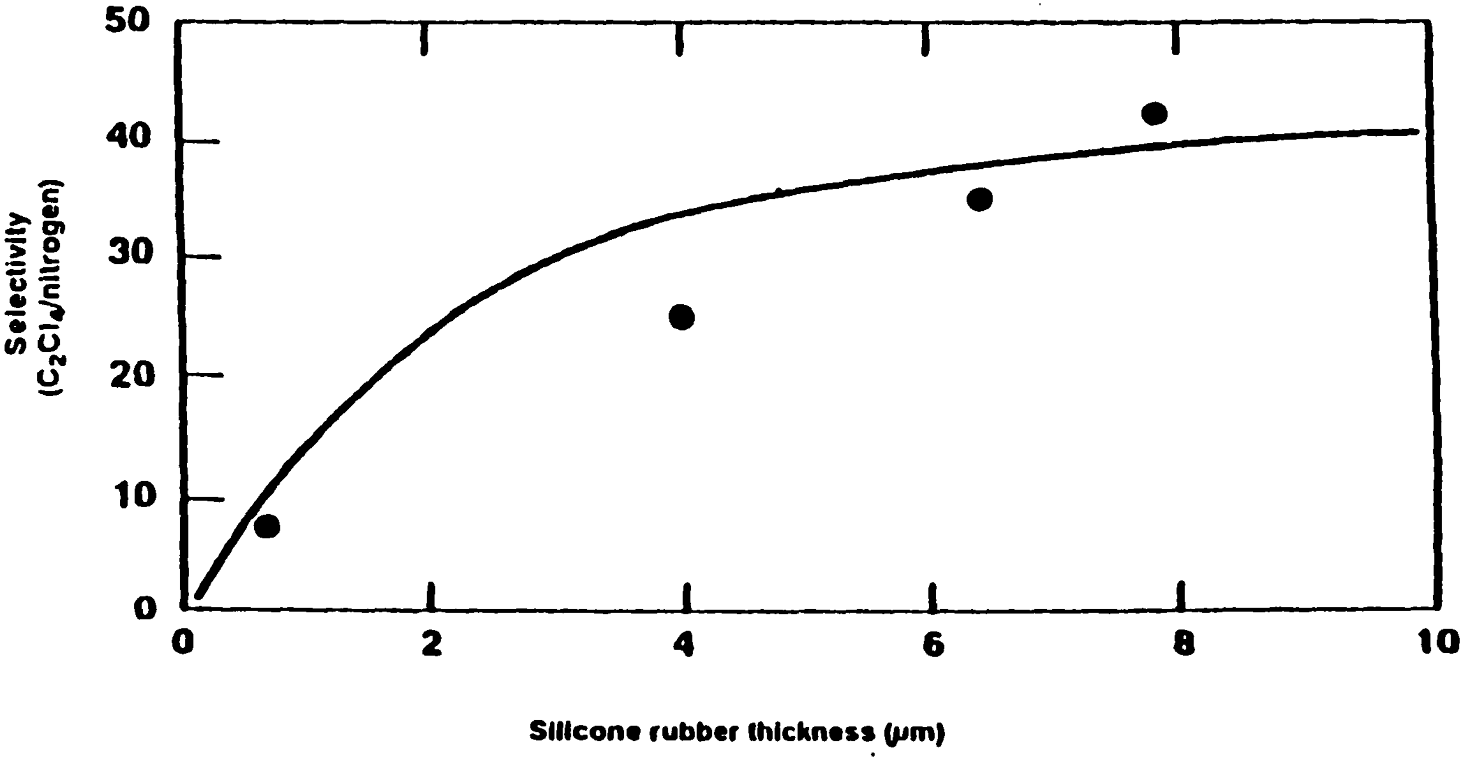


Figure 5.5 Comparision of the effect of the different membrane thickness. The material of the tested membrane was silicone rubber.



Figree 5.6 Tetrachloroethylene/Nitrogen selectivety of silicone rubber composite membranes. The solid line is calculated based on Equation 5.6 [Baker and Wijmans, (1994)].

because the number of sticky collisions decreases with the increased surface to volume ratio of the membrane. This means that the sites for sticky collisions are sites for solution of VOC and are in the bulk of the membrane. So it follows that number of sticky collision will increase as the surface to volume ratio decreases because the site for solution of VOC will increase. It is at those sites enthalpy is released as a result of VOC to polymer bonding which providing the driving force for permeation.

In other words, the increased permeation of the VOC molecules through the thick polymer is due to the lowered activation energy because of the formation of a lower energy transition state complex. It is postulated that the transition state complex consists of the surface atoms, projections of the polymers in the bulk, and the VOC molecule. This complex contains a "channel" between the polymers through which the VOC molecules diffuse to a solution site. The atoms on the surface, subjected to unbalanced forces are drawn downward: the property is called surface tension. When the membrane is thin, the two surfaces are close together, and will be drawn toward each other. That will result in the twisting of the polymers, causing the activation energy to increase and making diffusion through the channels between the polymers more difficult.

Moreover, the thin film is delicate and needs a porous supporting material which provides mechanical strength but may further decreases the permeation of VOCs due to the low permeability of the support membrane [Bai, et al., (1995); Baker and Wijmans, (1994); Wang, et al. (1995)].

Thus, when choosing the film thickness, two factors should be balanced: to get high selectivities, thick film is preferred; in other hand, to make high-flux composite membranes, minimizing the thickness of the selective layer is necessary. From equation

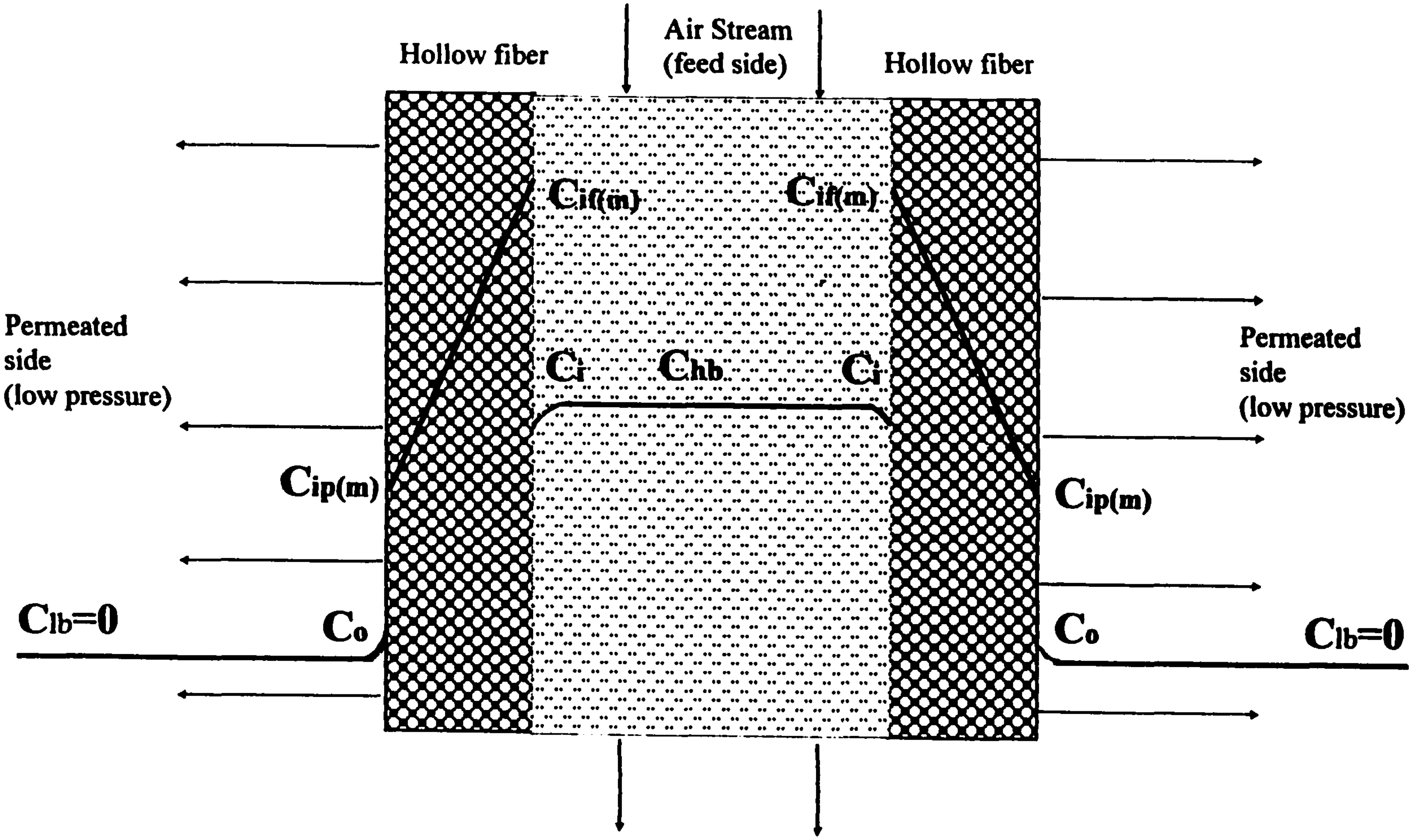
4.1, it is observed that the permeation flux of a permeant across the membrane is inversely proportional to the membrane thickness. The following equation has been suggested to determine suitable thickness of the selective layer of a composite membrane to achieve a desirable selectivity [Baker and Wijmans, (1994)]:

$$\alpha_{i/j} = \frac{\delta_1 / P_{1(j)} + \delta_2 / P_{2(j)}}{\delta_1 / P_{1(i)} + \delta_2 / P_{2(i)}} \qquad (5.6)$$

where δ_1 and δ_2 are the thickness of the support layer (1) and selective layer (2), respectively; and $P_1(i)$ and $P_2(i)$ are the permeabilities of the support layer and the selective layer, respectively.

5.3.2 Kinetics of the Membrane Enrichment of VOCs

In a non-porous membrane permeation process, mass transfer of a VOC occurs in three stages: (1) from the bulk gas through a gas film; (2) through the membrane wall; and (3) from the membrane wall through a gas film into the bulk stripping gas. To describe a VOC permeation process in the hollow fiber membrane, the solution-diffusion model is adopted. Most of the membrane module used in this study contained a number of hollow fibers assembled in a shell-and-tube type configuration. The resistances in series approach can be utilized to identify the role of various mass transfer resistances for the transfer of VOC molecules under non-reactive conditions [Nguyen, et al., (1991); Ji, et al., (1994); Wijmans, et al. (1996)]. Typical VOC concentration profiles in the hollow fiber membrane module are shown in Figure 5.7. When air stream containing VOCs continuously passes through a membrane permeator, the permeation rates in terms of an overall mass transfer coefficient R can be written as following expression:



Firue 5.7 Typical VOC concentration profiles in the hollow fiber membrane module

$$J = R 2\pi r_o lN(C_{hb} - C_{lb}) \tag{5.7}$$

If the permeation rate in terms of the individual mass transfer coefficients, then it can be expressed as following:

$$\begin{aligned} J_g &= R_g 2\pi r_i lN(C_{hb} - C_i), \\ J_m &= R_m 2\pi r_{lm} lN(C_{if(m)} - C_{ip(m)}), \\ J_v &= R_v 2\pi r_o lN(C_o - C_{lb}), \\ J_g &= J_m = J_v \end{aligned} \tag{5.8}$$

The solution-diffusion model also assumes that the following equilibrium expressions existed at the interfaces:

$$\begin{aligned} C_{if(m)} &= K_f C_i, \\ C_{ip(m)} &= K_p C_o \end{aligned} \tag{5.9}$$

Since a high vacuum is applied on the permeated side of the membrane, the concentrations in the permeated side: C_{lb}, C_o, and $C_{ip(m)}$ are assumed zero. Then, the relationship between the overall mass transfer coefficient and the individual coefficients will be obtained by rearranging above equations:

$$\frac{1}{R} = \frac{r_o}{R_g r_i} + \frac{r_o}{K_f R_m r_{lm}} \tag{5.10}$$

In this equation, the gas phase film resistance R_g can be calculated from a traditional solution for the gas flow in tubes, and the product of $K_f R_m$ can be obtained experimentally. Then the mass flux of the VOC can be obtained.

However, for the MPCS system, the experimental results show that with increased sampling time, the enrichment of VOC was changed (Figure 4.11). This indicates that the permeation rates change with time. In order to study the kinetic behavior in MPCS system, a non-steady-state time-mass flux relationship is adopted [Beckman, (1994)] and the time dependence of the VOC permeation flux at the membrane outlet in the sampling system can be expressed by the following equation:

$$J(t) = \frac{2\pi\, r_i lNCP}{\delta}\left[f(y) - \lambda\, f\left(y - \frac{P\Delta t}{\delta^2}\right)\right] \tag{5.10}$$

in which,

$$y = \frac{Pt}{\delta^2} \tag{5.11}$$

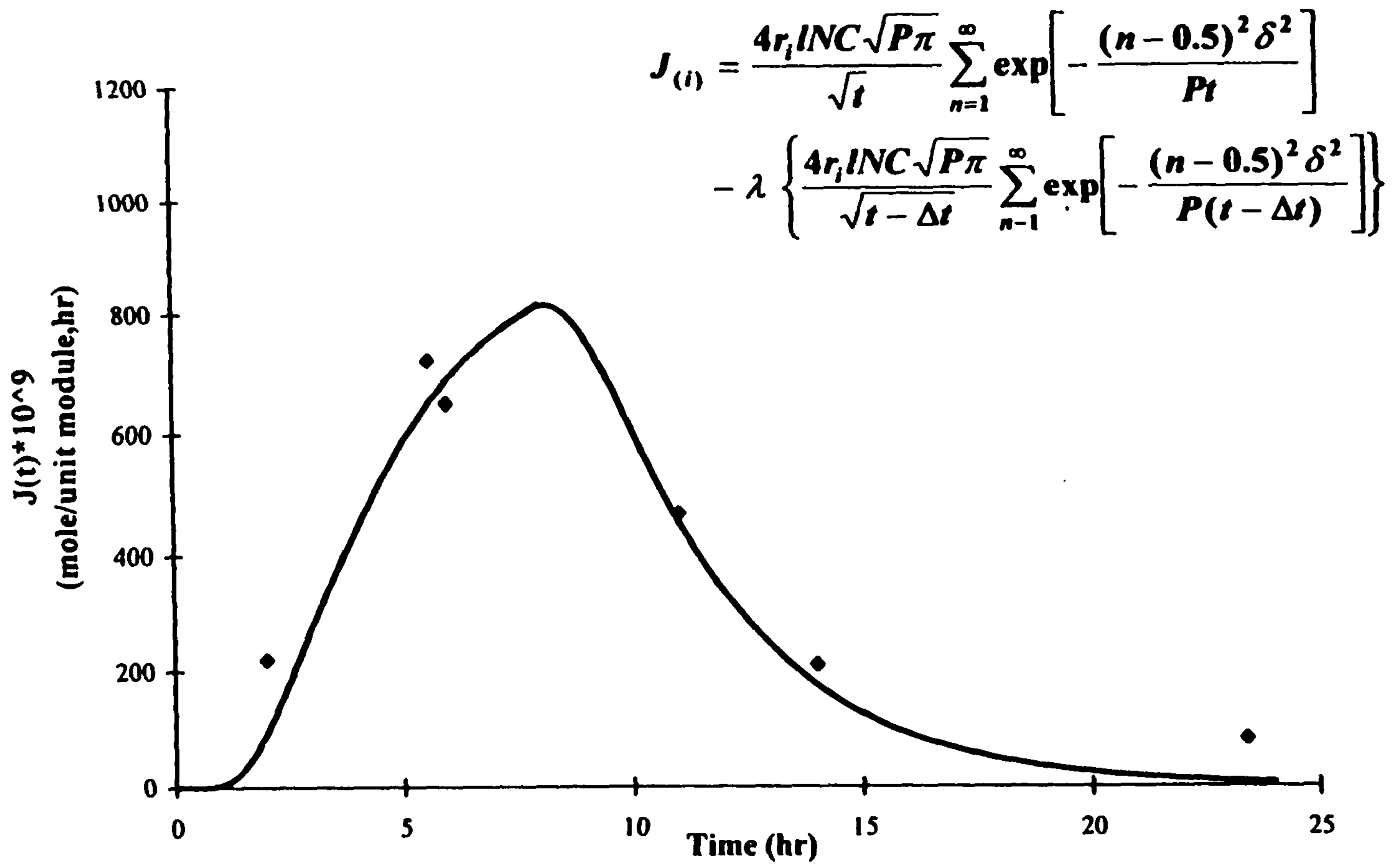
and

$$f(y) = \frac{2}{\sqrt{y\pi}}\sum_{n-1}^{\infty}\exp\left[-\frac{(n-0.5)^2}{y}\right] \tag{5.12}$$

When $y < \frac{P\Delta t}{\delta^2}$, $\lambda = 0$, the curve is in the ascending portion. And when $y > \frac{P\Delta t}{\delta^2}$, $\lambda = 1$, the curve is in the descending portion. Substituting the equations 5.11 and 5.12 into the equation 5.10, the time dependent permeation rate for MPCS system can be calculated by the following equation:

$$\begin{aligned} J_{(t)} &= \frac{4r_i lNC\sqrt{P\pi}}{\sqrt{t}}\sum_{n=1}^{\infty}\exp\left[-\frac{(n-0.5)^2\delta^2}{Pt}\right] \\ &-\lambda\left\{\frac{4r_i lNC\sqrt{P\pi}}{\sqrt{t-\Delta t}}\sum_{n-1}^{\infty}\exp\left[-\frac{(n-0.5)^2\delta^2}{P(t-\Delta t)}\right]\right\} \end{aligned} \tag{5.13}$$

A comparison between experimentally obtained and model predicted time-dependent permeation rates for Toluene is presented in Figure 5.8. The concentration of the Toluene in air stream was 300 ppbv and a single fiber membrane (15 cm long) permeator was used. The permeability of Toluene was obtained from the publication by Baker [Baker, et al. (1987)]. It can be seen in Figure 5.8 that the permeation rates of VOCs in the MPCS



$$J_{(t)} = \frac{4r_i lNC\sqrt{P\pi}}{\sqrt{t}}\sum_{n=1}^{\infty}\exp\left[-\frac{(n-0.5)^2\delta^2}{Pt}\right] - \lambda\left\{\frac{4r_i lNC\sqrt{P\pi}}{\sqrt{t-\Delta t}}\sum_{n=1}^{\infty}\exp\left[-\frac{(n-0.5)^2\delta^2}{P(t-\Delta t)}\right]\right\}$$

Figure 5.8 The permeation flux at the membrane outlet as a function of time. The points represent expermental data and the line was calculated using Equation 5.13.

system could be predicted using Equation 5.13. The data from the experiment appear to fit this model. Thus this mathematical approach can be used to determine a suitable sampling time to achieve a highest enrichment of VOC.

Furthermore, by differentiating Equation 5.10, a expression for the permeation rate change with time also can be calculated as follows:

$$\frac{dJ}{dt}=\frac{2\pi\, r_i lNCP}{\delta}\left\{2\sum_{n=1}^{\infty}(-1)^{n+1}n^2\pi^2\left[\exp(-n^2\pi^2 y)-\lambda\exp(n^2\pi^2 y-n^2\pi^2\frac{P\Delta t}{\delta^2})\right]\right\} \tag{5.14}$$

5.3.3. Application of the MPCS System

The application of this new sampling device based on membrane permeation technique was carried out by collecting real ambient air samples.

5.3.3.1 Collecting Real Samples Using MPCS System: Before sampling, all canisters were first cleaned by evacuating and flushing with zero grade air. This process was repeated three times. Then the canisters were evacuated to approximately -29 inchHg and then connected to the membrane permeators. The samples were collected from ambient air at one atmosphere and room temperature at three different sites: Site #1 was a garage of a single family house (about 100 square meters, usually parking two trucks) located at #127 Beech street, Kearny, NJ; Site #2 was a basement parking lot of a apartment complex, approximate 5000 square meters with no window or vent system, located at #425 Mt. Prospect Ave., Newark, NJ; the Site #3 was a hood in a chemical research lab for preparing chemical samples, which was temporally shut off and located in room 311, ATC building, NJIT, NJ. In order to reduce sampling time and use maximum area of membrane, passive sampling was used. An advantage of passive sampling was that no additional air sampling equipment such as pump is required. After sampling, all canisters were brought back to the lab for measurements using a valve-multibed-microtrap-GC (VMMGC) analytical system.

5.3.3.2 The Performance of the VMMGC Analytical System: An analytical system (VMMGC) was designed for analyzing the trace level VOCs in the low pressure canister after sampling by the MPCS device. Before running the real samples, accuracy and precision were first determined to evaluate the performance of this analytical system.

The performance of the VMMGC system was evaluated by running three times low ppbv gas standards which contained 0.07 ppbv of Toluene, 0.15 ppbv Acrylonitrile, and 0.15 ppbv Ethylacrylate. First, the air sample was drawn by a vacuum pump to pass through Carbontrap^{TM} C, B, and last Carbosieve^{TM} S-III. If large molecules get trapped in strong adsorbents such as Carbosieve^{TM} S-III, it is not easy to desorb them quantitatively. Therefore, at the injection position, (desorption mode), the direction of the purge gas flow was reversed, that is from CarbosieveTM S-III to CarbontrapTM C, otherwise, heavy VOCs might be retained in the adsorbents which had larger surface area. The backflush sample collection system used for analyzing VOCs in the canister is shown in Figure 5.2. In Figure 5.2, solid lines with arrows show the reverse gas flow directions during the sample collection, and broken lines with arrows show the normal flow directions used during the GC analysis. During the sample collection, a vacuum pump (P) is used to pull sample from the canister (CN) into the multibed microtrap (MT) and the GC analytical column (CL) is backflushed with additional carrier gas. After sample collection, the normal flow directions resume, and carrier gas flows from left to right through the microtrap. The microtrap was a thin wall small diameter tubing and could be heated very quickly. Thus a “concentration pulse” could be generated for the GC injection, indicating that the microtrap served here not only a concentrator for adsorbing VOCs but also a injector for GC injection.

The chromatograms for acrylonitrile, ethylacrylate, and toluene obtained using VMMGC analytical system are presented in Figure 5.9. The relative standard deviations of three runs were 7.6%, 9.6%, and 8.9% for toluene, acrylonitrile, and ethylacrylate, respectively. The linear characteristics of the analytical system was also investigated by running different concentration levels of toluene, acetone, and benzene. The calibration curves for those VOCs are presented in Figure 5.10. The initial testing showed that the analytical system was in good working condition and could be used to detect and quantitate low ppbv level VOCs in a low pressure canister.

5.3.3.3 Analyzing Real Samples Collected by MPCS Device: To compare the enrichment effect of the membrane permeator, canister samples were collected simultaneously with and without the membrane permeator. One set of canisters used the membrane permeator, the other, collected sample in conventional way without the membrane. Sampling and analytical conditions were identical for both sets.

During analysis, a 1200 ml air sample was draw through the microtrap at an average flow rate 20 ml/min. A high precision digital pressure gauge installed at the outlet of the canister was used to measure the canister pressure before and after analysis.

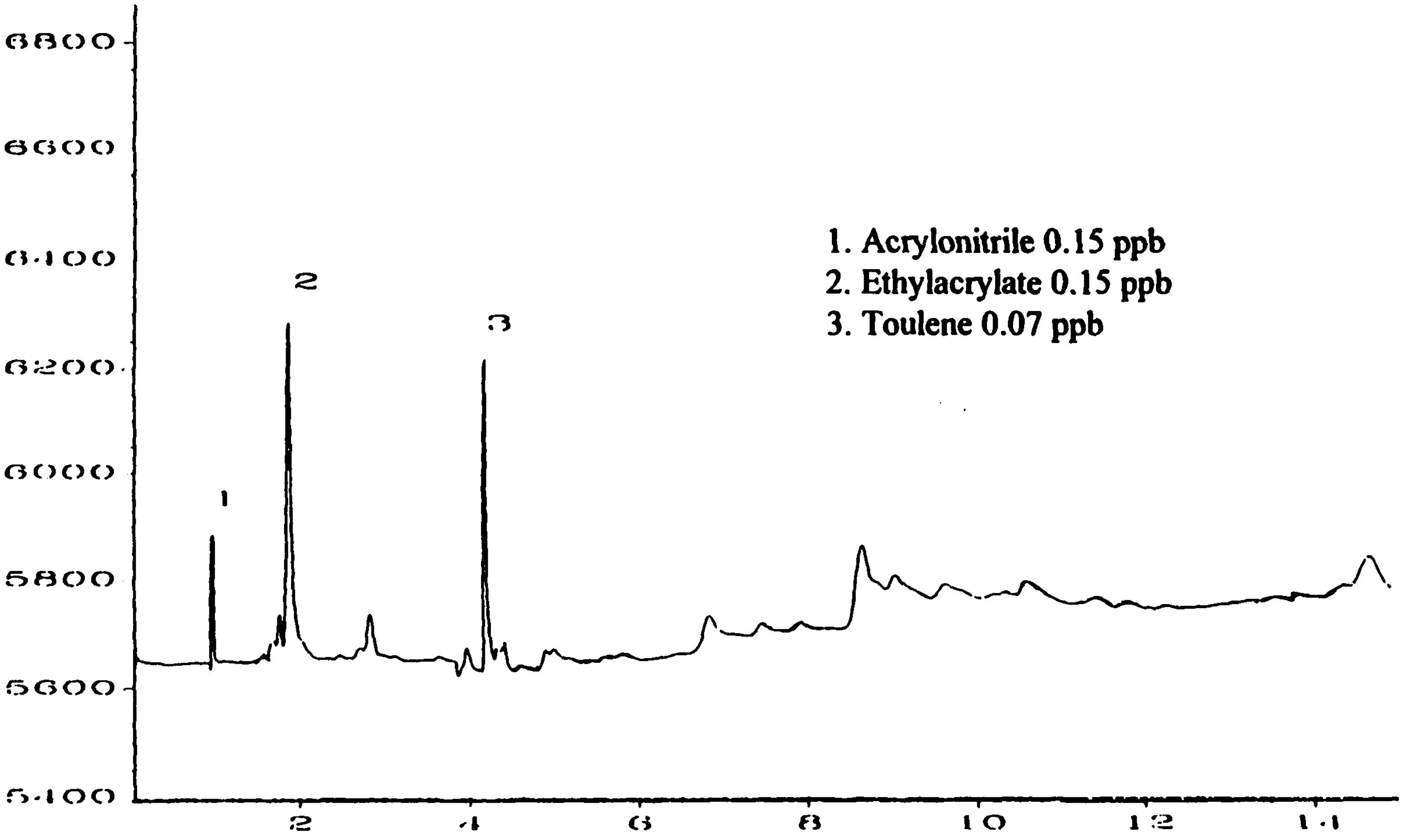
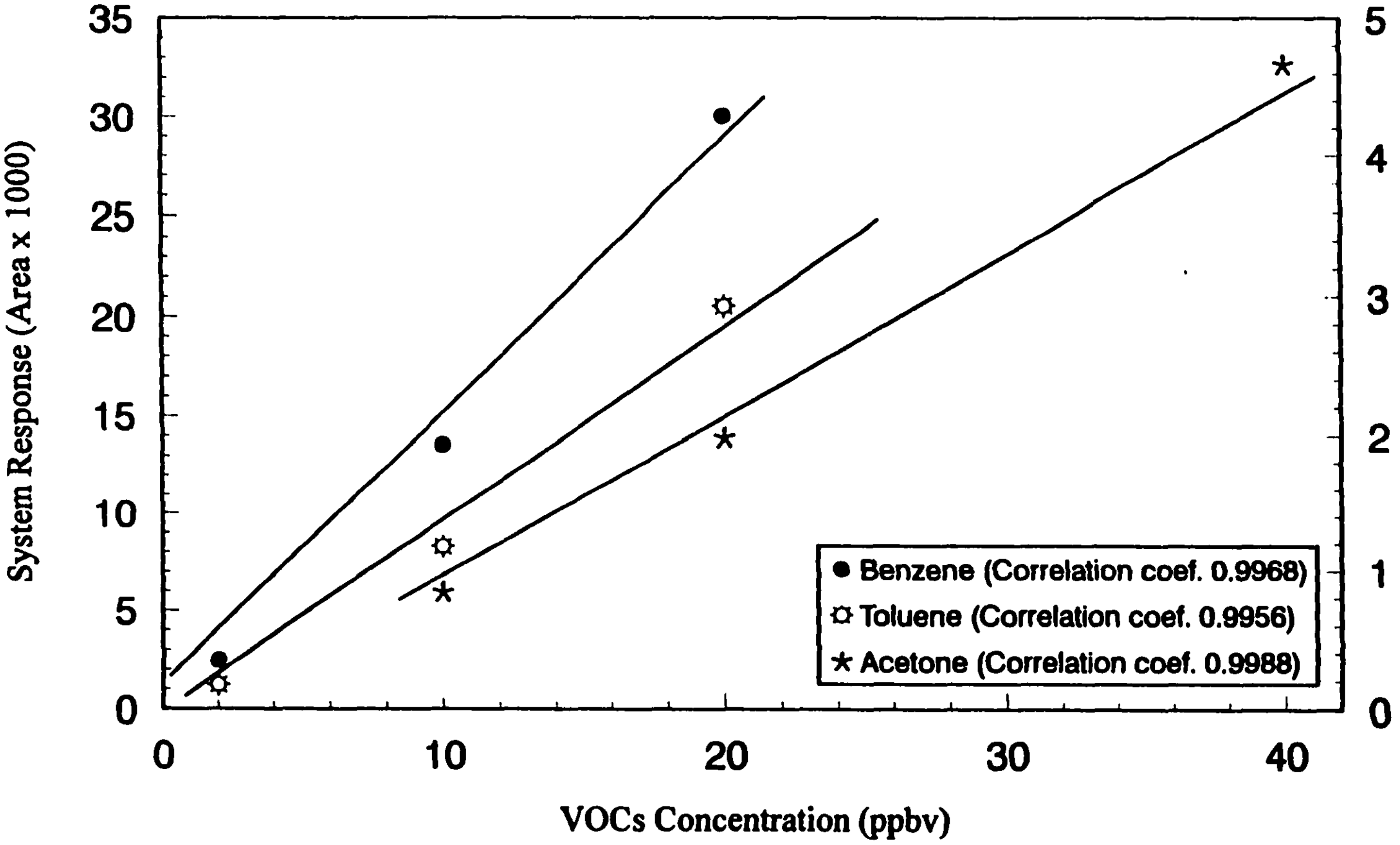


Figure 5.9 Chromatogram of the standard gas at low ppbv level. The sampling volume was 1200 ml. The pulse time was 4 seconds and the pulse current was 50 A.



Figur 5.10 Calibration Curve using VMMGC analytical system. The sampling volume was 1200 ml and the pulse timeof the microtrap was 4 seconds at the pulse current 50 A.

The total sampled volume was also computed based on the pressure reading. After sampling, the valve was switched to injecting position and nitrogen was first used to purge and clean the valve, microtrap, and transfer line. And then, a heat pulse was applied to the microtrap and VOCs were desorbed into the GC column. The chromatograms for those air samples are presented in Figure 5.11, 12 and 13. The two chromatograms are from two canisters, one with the membrane permeator, and the other without. The chromatograms are also presented in the same scale, so that they can be directly compared. It can be clearly seen that in each case the sample with the membrane permeator showed a higher response indicating enrichment of VOCs in the canister.

The chromatograms in Figure 5.11, and 12 are from samples collected in the garages and appear to show the gasoline patterns, usually called total petroleum hydrocarbons (TPH). The experimental results indicate that TPH existed in the ambient air for both sites (Site $^{\#}$1 and Site $^{\#}$2). Figure 5.11 and 12 also indicate that some diesel might present in the Site #1 and the concentrations of TPH were enriched approximate three times higher using membrane permeator than directly using a canister. Canister samples with and without the membrane permeator were collected in duplicate. The relative standard deviation was 11.6% for MPCS and 9.9% when sampled directly. The auto exhaust is a complex sample and high resolution chromatography was not performed to identify the different compounds. In the conventional EPA methods, total area account for all peaks is used to calculate the concentration of TPH.

The samples collected in the fume hood contained fewer compounds as this hood was mainly used to store solvents. The analytical results for the fume hood air analysis are presented in Table 5.5 and Figure 5.13. The investigation shows that low level organic solvents such as Methanol, Acetone, Methyl ethyl Ketone (MEK), Benzene, Toluene, and Xylene presented in the fume hood. Once again, the membrane permeator showed significant enrichment of the VOCs. The enrichment factor was calculated based on the results obtained from direct canister sampling. The relative standard deviation based on duplicate canister sample is also presented in Table 5.5. The RSD appears to be higher for the polar compounds.

Table 5.5 The experimental results for the samples collected in the Site #3

Organic Compound	Enrichment Factor E%	Relative Standard Deviation
Methanol	270	10
Acetone	210	13
MEK	270	5.4
Benzene	320	7.3
Toluene	370	6.0
Xylene	380	3.0

5.4 Summary

The MPCS has been evaluated by collecting real ambient air samples. The results demonstrated that VOCs can be concentrated by membrane permeation. A passive sampling system that incorporates a permeator design which uses the vacuum in the canister to draw a concentrated sample into the canister appeared to function quite effectively.

It was observed that the thicker membrane provided higher selectivity and consequently greater enrichment of VOCs. However, the sample flow was higher when thinner membranes were used. Optimization of film thickness is necessary to satisfy high selectivity and high permeation flux.

To establish MPCS system as a leading technique for the trace level VOCs collection in the ambient air, further developments are required in the membrane technology. Upon the availability of other selective membrane materials, a wider range of organic compounds can be collected and analyzed using this method.

We have in this study been able to articulate the questions that have to be answered to develop a model that will follow scientific principles and will be expressed in analytical equations which will make it possible to change this field from an art to a predictable science and technology.

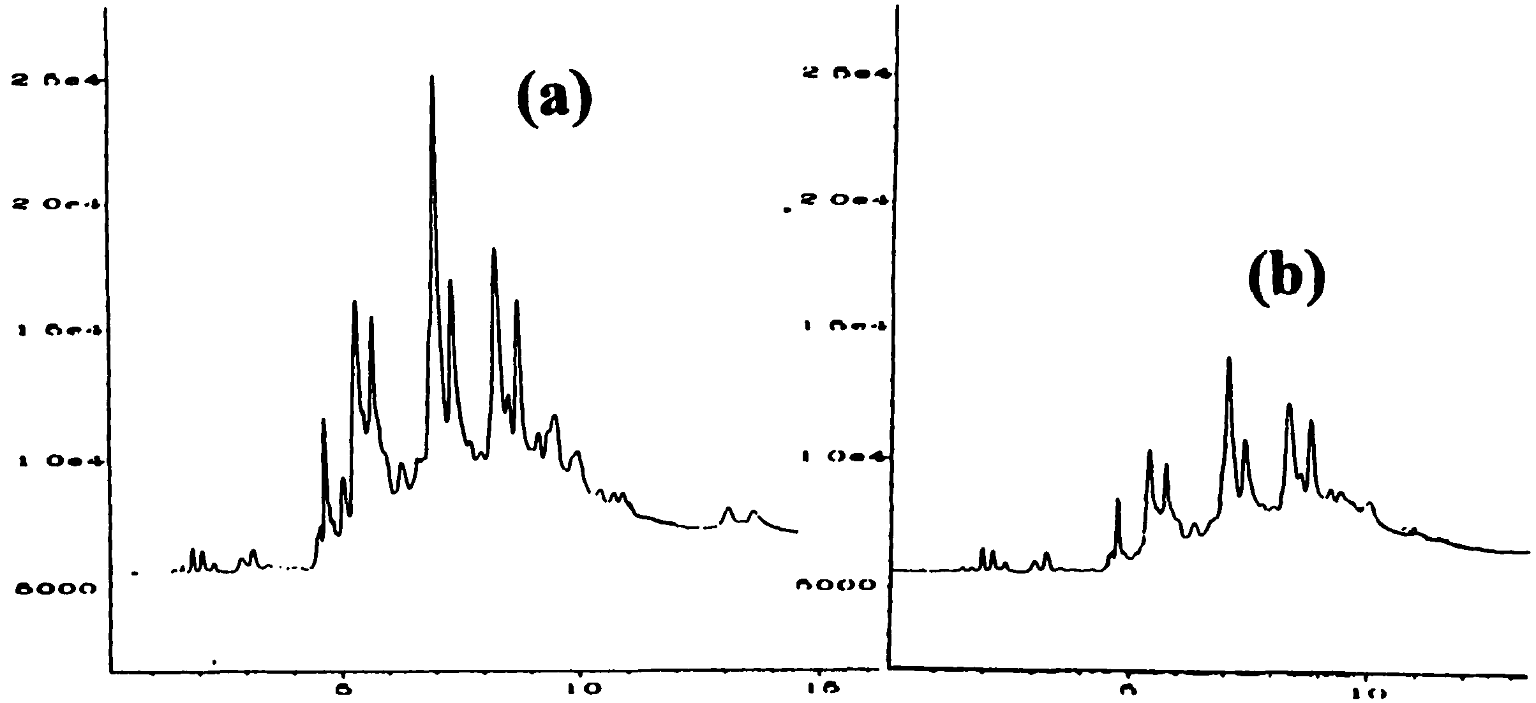


Figure 5.11 Chromatogram of TPH in the indoor ambient air at Site #1: (a) Sample was collected using MPCS sampling system; (b) Sample was collected using a canister alone.

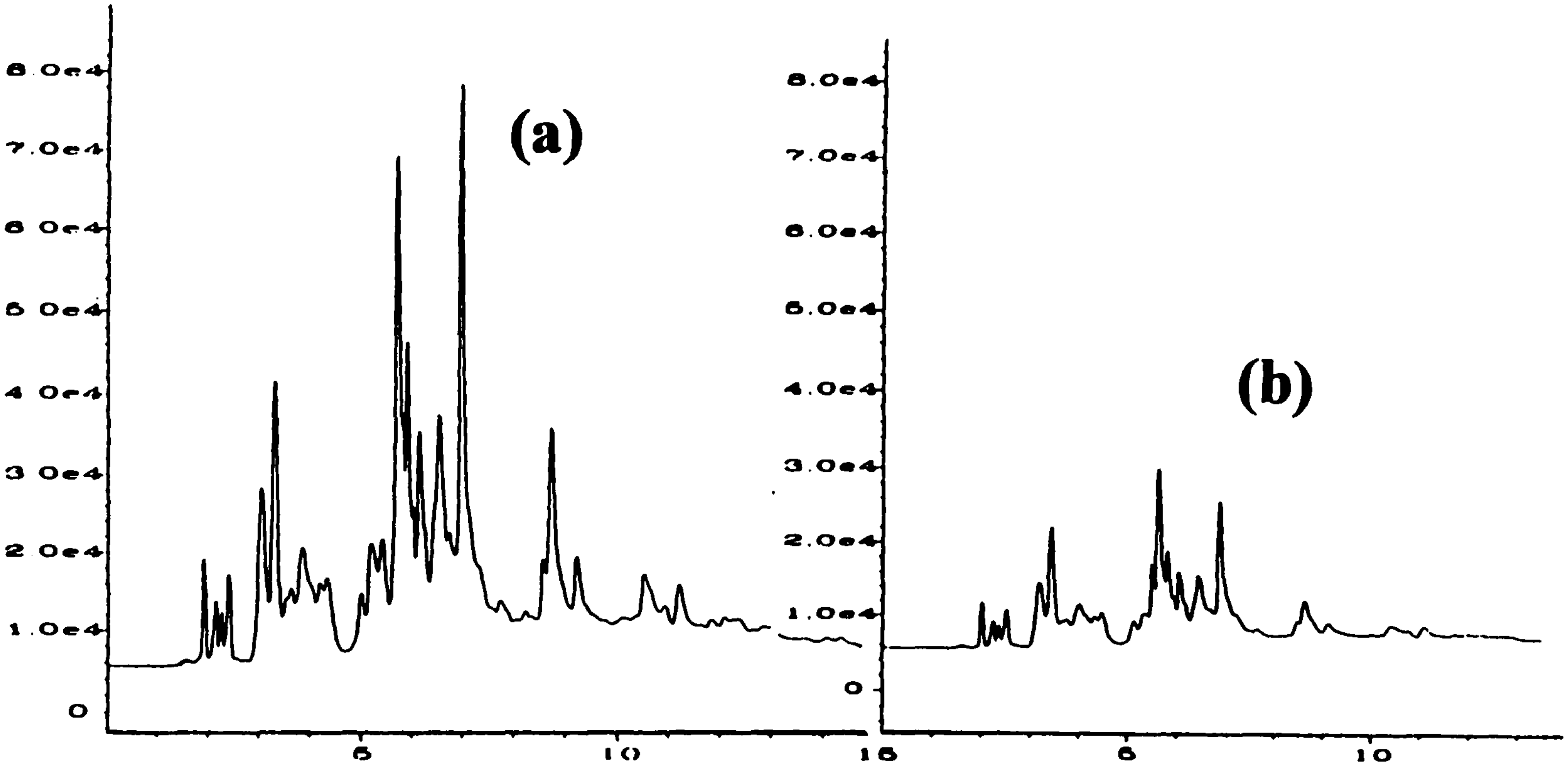


Figure 5.12 Chromatogram of TPH in the indoor ambient air at Site #2: (a) Sample was collected using MPCS sampling system; (b) Sample was collected using a canister alone.

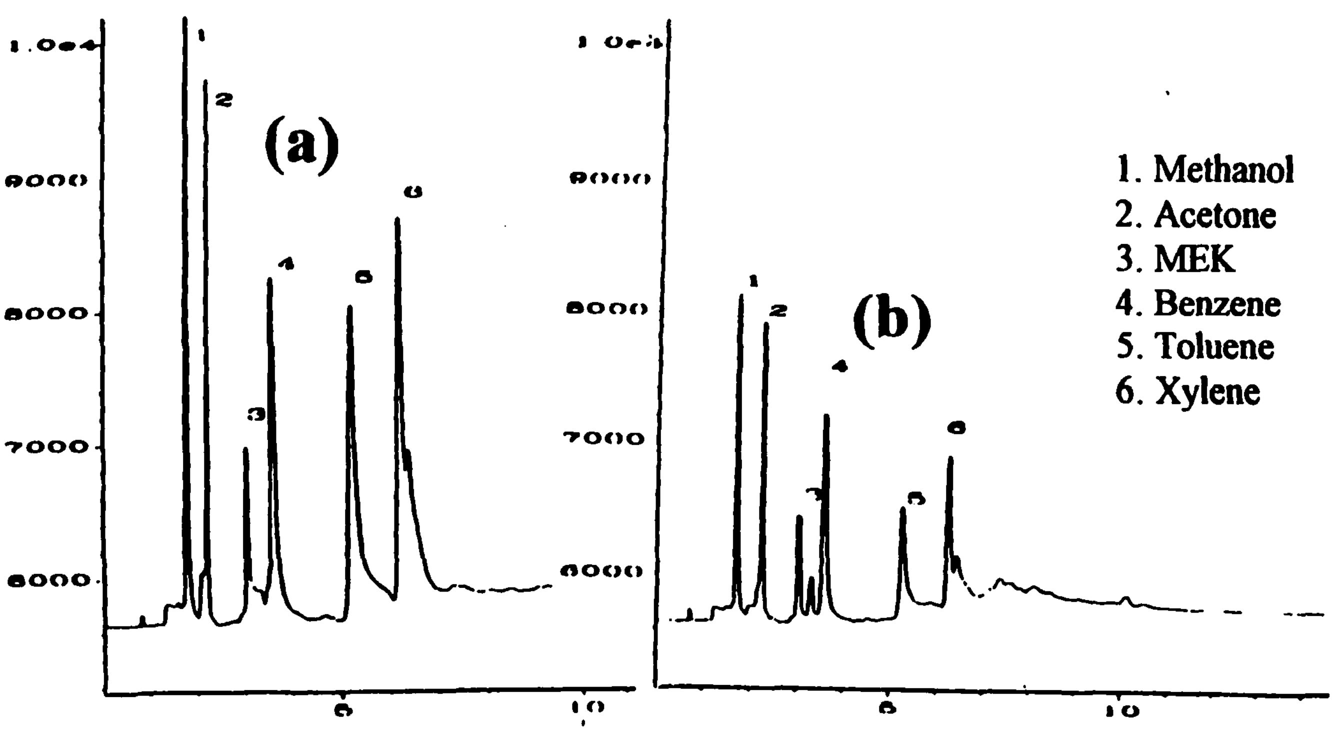


Figure 5.13 Chromatogram of organic solvents in the fumehood air at Site #3: (a) Sample was collected using MPCS system; (b) Sample was collected using a Canister alone.

CHAPTER 6

ON-LINE MEMBRANE EXTRACTION MICROTRAP GC SYSTEM FOR CONTINUOUS MONITORING OF VOCs IN AIR EMISSIONS (PART I: PERFORMANCE AND OPTIMIZATION)

6.1 Introduction

One of the most serious aspects of air pollution is the problem of volatile organic compound (VOC) emissions. These VOCs, in addition to being potentially hazardous to human health, are also key contributors to the formation of smog. Regulations regarding VOCs become increasingly stringent both at national and international levels. Moreover, all industries are required by the Community Right to Know Act included in the Superfund Amendments and Reauthorization Act to report to authorities about any accidental and routine releases of listed chemicals.

It is clear that monitoring of VOCs is of utmost importance for compliance with those regulations. These regulations are also requiring manufacturing facilities to implement a variety of VOCs control devices such as carbon adsorption, condenser systems, wet scrubbing, biodegradation, membrane separation, and incineration. When applicable, incineration is a method of choice because it converts VOCs to carbondioxide and water.

Sensitive, continuous monitoring methods are needed to provide real-time (or near-real time) identification and quantitation of emissions from these control devices so that proper functioning of the devices can be ensured. The conventional air monitoring methods either use sorbent cartridges (e.g., EPA Method TO1) or use whole air sampler such as a canister (e.g., EPA Method TO14). Either of these approaches involves collecting air sample in the field followed by analysis in the laboratory and can not be used for continuous, on-line analysis. Thus, there is a real need for instrumentation that can be used to carry out automated, on-line analysis to provide information on a continuous basis that can be used for process control as well as for meeting regulatory compliance.

The major component of an on-line analyzer is the sampling and injection device. In air analysis, conventional multiport valves are the most popular injection device used in systems. Such as Cone and coworker's total hydrocarbon continuous emission monitor [Cone et al. (1989)]. Valves can automatically make injections from a sample stream intermittently into a GC column. However, the sample valves only can withdraw a small fraction of the sample stream for injection into the GC, which results in a small sample quantity and limits sensitivity. Injecting a larger sample quantity causes excessive band broadening and degrades chromatographic resolution. Therefore, it is necessary to develop a device which can concentrate the analytes from a large volume prior to GC. Infrared analyzers using narrow bandpass interference filters and on-line mass spectrometers have been used many years for ambient air and process stream monitoring, which provide fast response and both qualitative and quantitative information [Wilks, (1991); Ortiz and Woodside, (1991)]. However, moisture inference and band overlap are very serious problems for those techniques in environmental applications. Recently, membrane introduction mass spectrometry techniques have been received much attention.[Lapack, Tou, and Enke, (1990)]. Nevertheless, a typical environmental sample may contain dozens of compounds. Without chromatographic separation the identification and quantitation of these VOCs from complex environmental sample would be very difficult, if not impossible. Moreover, a variety of sensitive and selective detectors including MS and FTIR are available for GC.

Our laboratory has initiated a investigation to explore the possibility of combining membrane technique with gas chromatography technology for continuous monitoring of VOCs in air [Zhang, (1994)]. Although the initial study was carried out mainly in a quanlitative fashion, the experimental results have shown that this monitoring device may potentially be able to monitor VOCs at ppb levels.

The objective of this study is to expand the initial work and study will be carried out in more detail at ppbv levels. In this approach, a technique referred to as on-line membrane extraction microtrap gas chromatography (OLMEM) is developed for continuous monitoring of trace level VOCs in air emissions.

Most emission streams are complex mixtures and along with VOCs contain large quantities of other components. For example, combustion sources contain large quantities of H_2O vapor, CO_2, SO_2, NO_x etc. Some of these background gases may interfere with VOCs analysis and/or reduce the lifetime and ruggedness of the capillary column. Thus, those interferences must be removed before analysis.

In the approach described here, the VOCs are allowed to selectively permeate through a membrane into an inert gas. Then the permeated VOCs are concentrated and injected into a GC using a very small sorbent trap referred to as microtrap.

On-line Microtrap: The concentration of VOCs in air emissions and consequently in the permeate stream can be quite low at the parts per trillion (ppt) to parts per million (ppm) levels. Thus it is necessary to concentrate the analytes from a large volume prior to GC analysis. Direct injection of large samples into GC is not possible because of excessive band broading. Here, an on-line microtrap is used for sample preconcentration cum injection. Trace analytical application using the microtrap has been reported previously from our laboratory [Mitra and Lair, (1995); Mitra and Chen, (1993); Mitra, (1994)].

The microtrap is made by packing a small diameter tubing with an adsorbent. It is placed at the entrance to the GC column instead of the injector. The N_2 stream containing the VOCs passes through it. The analytes are trapped by the adsorbent while the N2 serves as the carrier gas. The microtrap can be electrically heated with a pulse of electric current so that the analytes desorb as a concentration pulse sharp enough to serve as an injection for GC separation. The system operation involves heating the microtrap at regular intervals of time, and corresponding to each injection a chromatogram is obtained. Due to its small size and low heat capacity the microtrap can be heated/cooled rapidly, and injection can be made every few seconds. The electric pulses are controlled by a computer.

Membrane Extraction of VOCs: Most trace analysis usually involves a separation step where the analytes are first separated from the environmental matrix. In a continuous, on-line application, the separation has to be carried out on-line in a continuous fashion. Membrane extraction of VOCs is partically attractive in this type of analysis because the membrane allows continuous, on-line extraction and stripping of trace VOCs from the complicated environmental matrix. Simultaneous extraction and stripping of VOCs can be taken place in one single step. The feature of simultaneous extraction and stripping removes the equilibrium limitation, consequently, increases the extraction efficiency. Thus, the near quantitative removal of VOCs from the feed stream is possible.

From the geometry of viewpoint, the membrane can be classified as porous, non-porous, and composite. The membrane selectivity may be due to a molecular mechanism, such as ultrafiltration, or a solution-diffusion mechanism, such as reverse osmosis, or both, such as nanofiltration membranes. In the first mechanism, species are separated by pressure-driven convective flow through small pores. In the solution-diffusion mechanism, permeants first dissolve in the membrane, and then diffuse through the membrane down a concentration gradient or partial pressure gradient. Here, a separation is achieved due to the difference in the amount of compounds which dissolves in the membrane and the diffusion rate through the membrane. Generally speaking, porous membranes offer low mass transfer resistance, but relatively low separation selectivity usually limited by Knudsen diffusion. Conversely, non-porous membranes show high selectivity but also high mass transfer resistance. In order to obtain both high permeability and selectivity, a composite membrane, microporous polypropylene hollow fiber coated with a thin layer of silicone, was selected in this study.

6.2 Experimental Section

The experimental system consists of the membrane module, the microtrap, and a GC/FID. The overall set-up used for the experiment is presented in Figure 6.1. The air sample flowed through the membrane module, inside the membrane fibers. Nitrogen (stripping

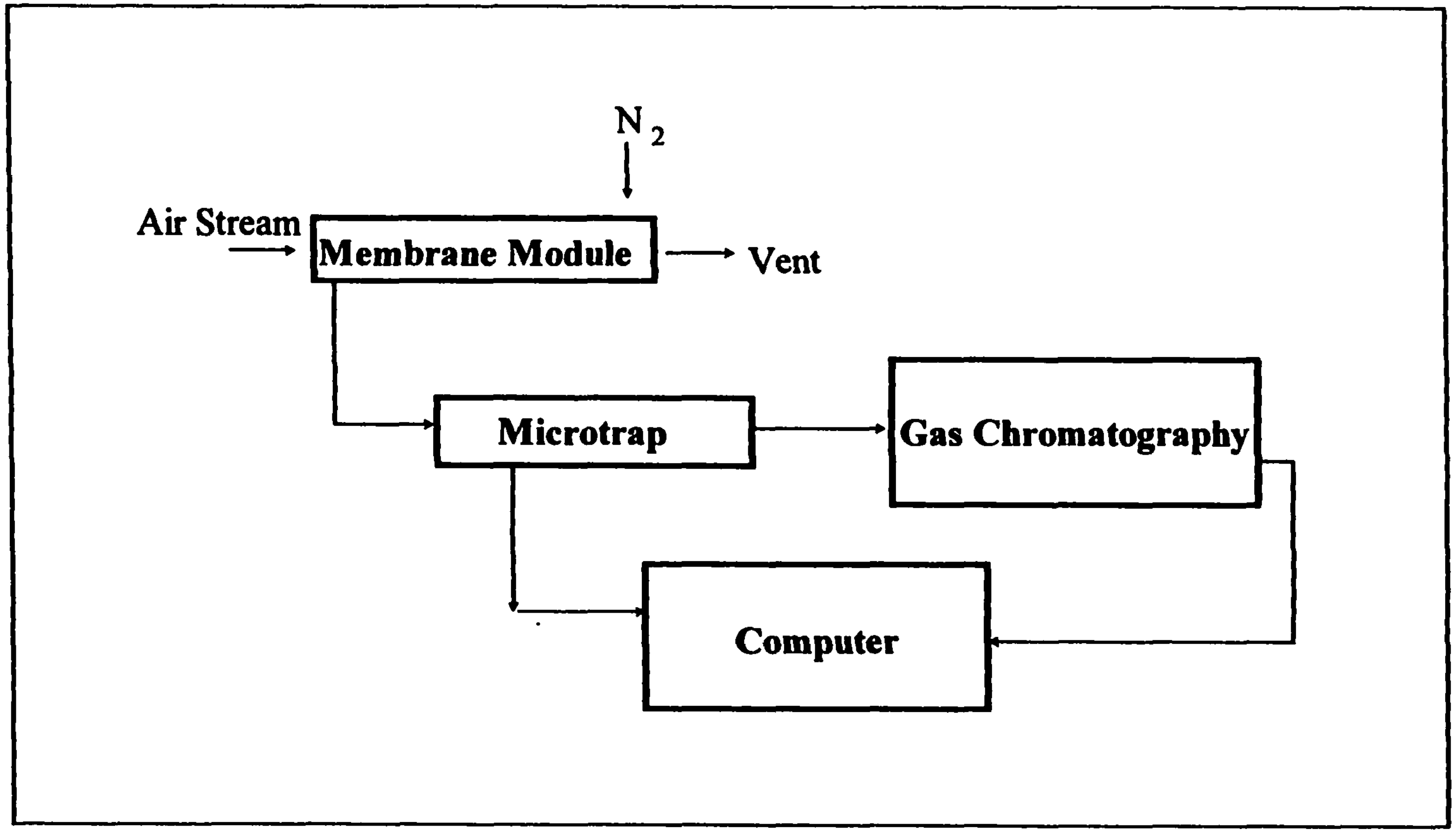


Figure 6.1 Schematic diagram of On-line Membrane Extraction Microtrap GC system.

gas) flowed cuntercurrent around the membrane fibers and carried the permeated VOCs from the membrane module to the GC column. Before entering the GC column, the VOCs were trapped by the microtrap. The microtrap was heated (or pulsed) at regular intervals. A chromatogram was obtained for each pulse.

The membrane module was constructed from a piece of 1/4" tubing with as many as twenty hollow fibers going through it.

A composite membrane: microporous polypropylene hollow fiber coated with 1 μm thick film of homolgenous silicone was mainly used in this study. The size of the composite membrane was 0.206 mm I.D. x 0.260 mm O.D. (Applied Membrane Technology, Minnetonka, MN, USA). The silicone membrane (0.305 mm I.D. x 0.635 mm O.D.) purchased from Dow Corning Corporation was also used in some investigations. The selective membrane material is a poly dimethylsiloxane elastomer. It is chemically, physically, and thermally stable.

The microtrap was constructed by packing a deactivated fused-silica lined stainless steel tubing (0.53 mm I.D.) with Carbotrap^{TM} C (Supelco Inc., Supelco Park, PA. USA).

The fused-silica microtrap was externally coated with electrically conductive paint and could be heated by passing current through it. The lengths of the microtraps were varied from 12 to 15 cm depending on the test requirements. Seven to ten amperes of current were used to heat the microtrap. The energy was supplied by a Variac (STACO Energy Products Co.) and the switching was done using a microprocessor controlled device built in house. The heating current to the microtrap could be turned on for a prespecified duration and at a fixed interval of time. Current pulses were applied any where between half minute to five minutes. The duration of each current pulse was between 0.5 to 1.5 second. Since the microtrap operation is quite fast and conventional thermocouples have low response times it is not possible to accurately measure microtrap temperature. A crude measurement using a thermocouple showed that temperature as high as 400 ^{0}C was reached in 2 to 3 seconds.

All the chemicals used in this experiment were chromatographic grade. Certified gas standards were made by Alphagaz (Morrisville, PA, USA). Different concentrations of samples were also made in the lab in a canister or in a small gas cylinder. In some experiments, diffusion tubes were used to generate a VOCs stream using the method published by Savitzky and Siggia [Savitsky and Siggia, (1972)]

A Varian GC (Model 3400) or a Hewlett-Packard 5890 Series II GC equipped with a flame ionization detector (FID) was used in this study. A 30 m long, 0.315 mm I.D, DB-624 column (J&W Scientific, Folsom, CA, USA) with a 1.8 μm thick stationary phase was used for separation.

The injection port of the GC was bypassed and the sample was introduced directly into the column through the microtrap. Nitrogen was used as the carrier gas and flow rates were between 5 and 10 ml/min. The temperature for detector was 250^0 to 280 ^{0}C and for injection port 150 ^{0}C. In the most cases, an isothermal program (80 ^{0}C or 100 ^{0}C) was used for the column separation. Typical flow rates for FID were: air 300 - 350 ml/min, H_2 25 - 30 ml/min, and make up gas Nitrogen 20 -30 ml/min. The data acquisition was done using HP 3365 Chemstation or HP 3396A integrator.

6.3 Results and Discussion

6.3.1 Performance of the OLMEM Monitoring System

6.3.1.1 Evaluation Using Gas Standards: The operation of the analytical system was demonstrated by continuously monitoring a standard gas mixture whose composition simulated the emission from a hazardous waste incineration. It contained 1 ppm each of benzene, toluene, ethylbenzen, trichloroethylene (TCE) along with combustion products such as CO_2, CO, SO_2 etc. A real combustion product collected from a hazardous waste incinerator was also used, which contained low ppbv levels of Methanol, Acetone, Benzene, and Toluene. During the test, the gas sample flowed continuously through the membrane module at the flow rate of 15 ml/min and the microtrap was pulsed every 3 minutes. The chromatograms of the organic compounds were obtained at each time a pulse was made (Figure 6.2). From Figure 6.2, it was observed that good precision in peak height, peak shape as well as retention time was obtained. Thus the membrane extraction process, the microtrap injections, and their combination were all reproducible. The factor that limits the frequency of analysis is the column separation time rather than the heating/cooling cycle of the microtrap so it is advantageous to reduce the separation time if analysis is to be done more frequently.

6.3.1.2 Calibration Curve and Method Detection Limit: The primary study had demonstrated that the OLMEM monitoring system worked effectively to monitor trace level VOCs in the emissions. The results obtained by this technique were in line with theoretical considerations. Experiments were also carried out to evaluate its figures of merit, such as linearity , method detection limit, precision, etc.

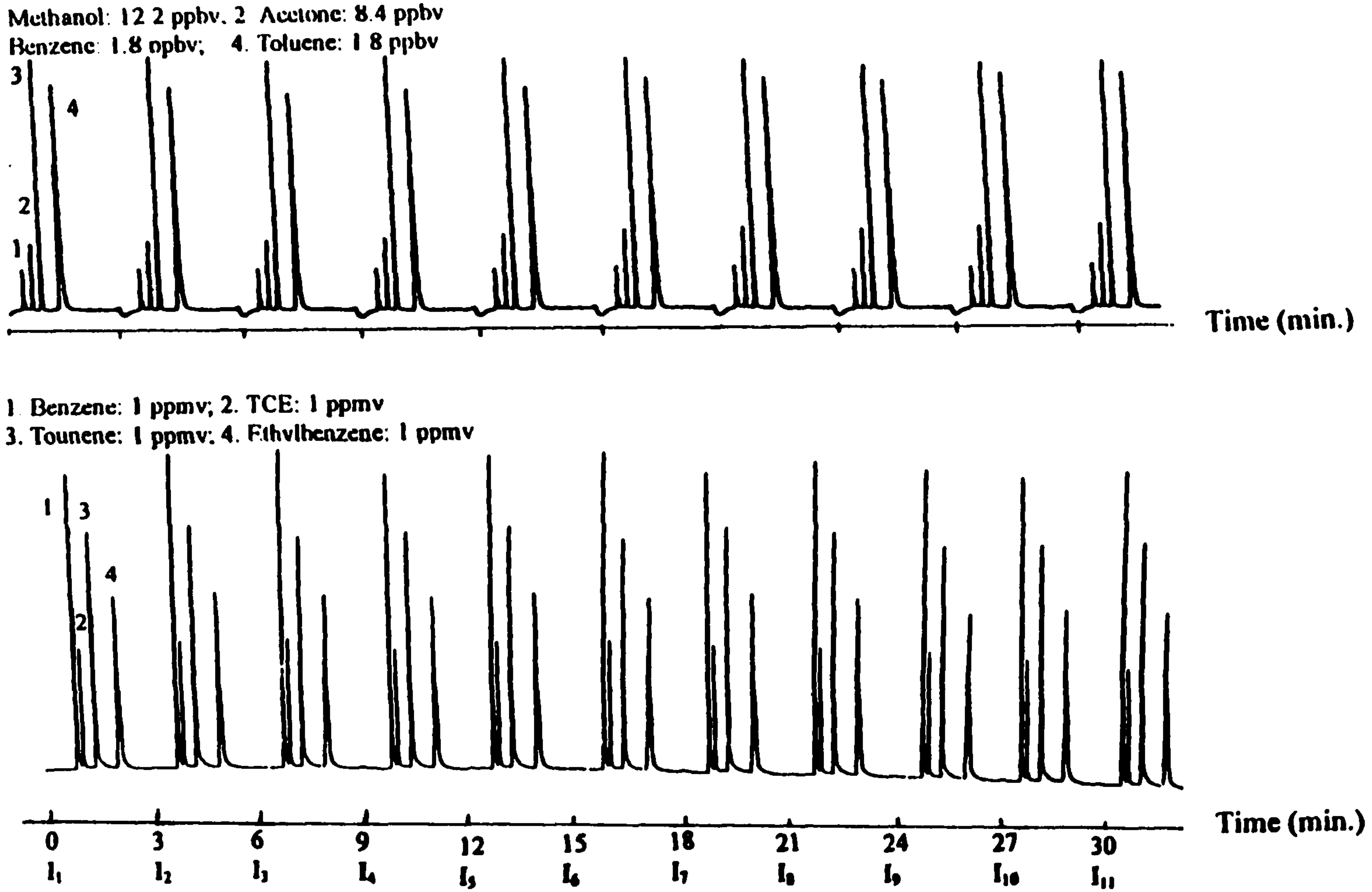


Figure 6.2 Continuous monitoring of the simulated stack gas containing VOCs, 10.9% oxygen, 9.27% carbon dioxide, 164 ppm sulfur dioxide, and 75 ppm carbon monoxide.I1, I2, I3.....are the microtrap injections corresponding to which the chromatogams are obtanined.

For the monitoring system linearity study, a series of standard gas mixture at concentration 5 to 300 ppbv were analyzed using OLMEM system. The calibration curves of acetone, benzene and toluene are presented in Figure 6.3. A linear relationship between system response and VOCs concentration was observed indicating that the membrane permeation process as well as the retention process in the microtrap were linear.

The method detection limits (MDL) for some VOCs were measured using standard EPA procedure (49 CFR Part 136, Appendix B). Here, the MDL was defined as the minimum concentration of a substance that could be measured with 99% confidence. The test compounds were benzene, toluene, trichloroethylene, and ethylbenzen which existed in the gas matrix along with other combustion products. The initial detection limits (test concentrations) of those compounds were estimated to about 0.5 to 2 ppbv based on the previous study, which corresponded to the OLMEM system signal to noise of approximately five from the GC/FID chromatograms.

According to the EPA procedure, a minimum of seven replicates of a sample with concentration between one and ten times higher than estimated MDL have to be tested. In this MDL study, The primary gas standard was purchased from Alphagaz and contained 1 ppmv of each Benzene, TCE, Toluene, and Ethylbenzen, respectively. Dilution in six steps were made using volume appropriate to generate eight replicate reference samples at about three ppbv. The standard used to calculate the concentrations of the samples was prepared from an independent set of dilutions of the same primary standard. The standard for quantitative determination contained 2.39 ppbv of each test analyte. The replicates and standard were sampled and analyzed using the OLMEM monitoring system in the exactly same fashion and a single membrane module was used in the experiment.

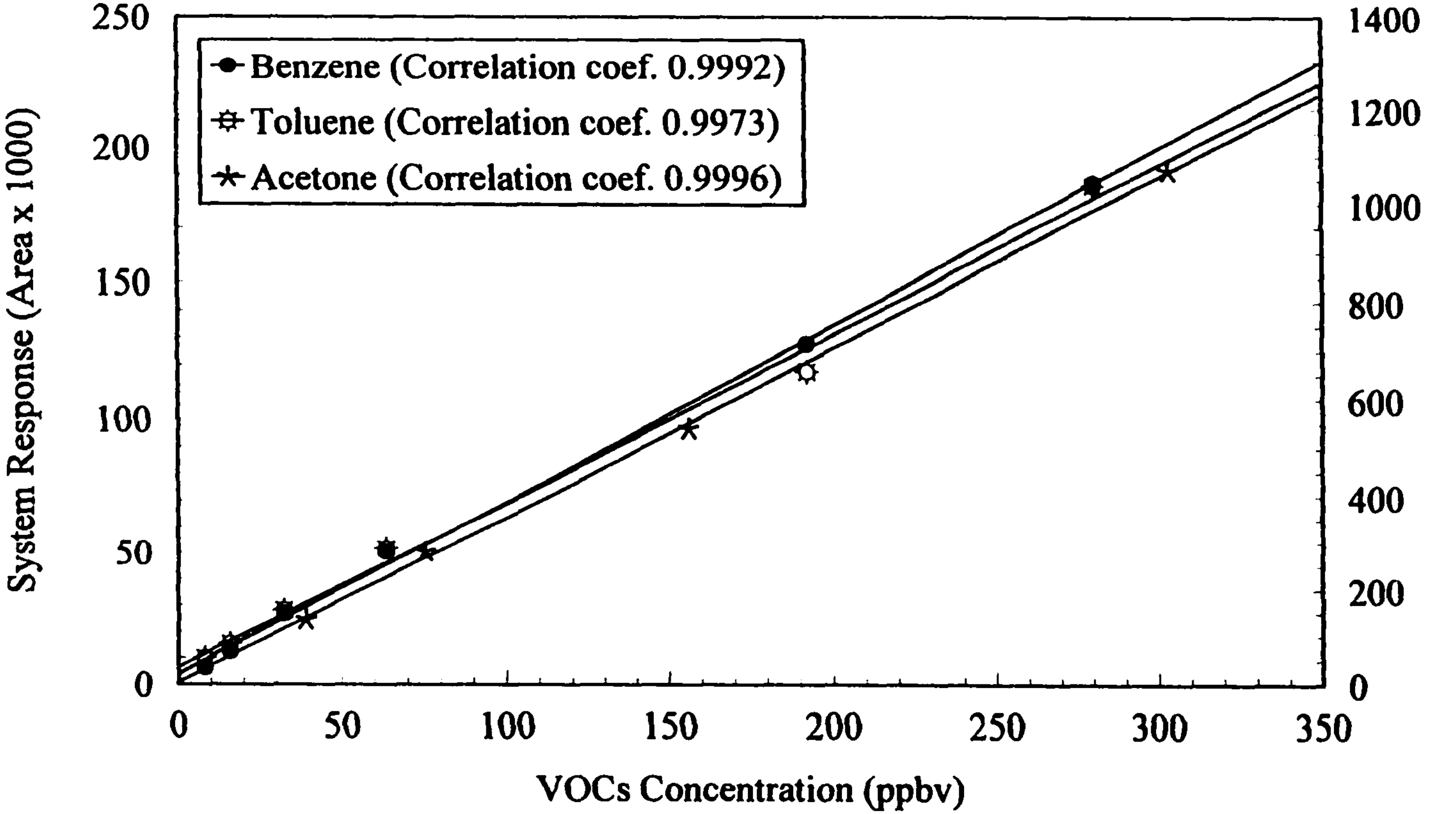


Figure 6.3 Calibration Curve. The pulse time was 1.2 seconds at current 30 A and the pulse interval was 3 minutes.

The variance and standard deviation of the replicate measurements were determined and the MDL was computed as follows:

$$MDL = sd * t \tag{6.1}$$

where: sd was the standard deviation of eight replicates, the student's t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of the freedom. The MDL and the results from the individual measurements including the concentration, mean value, standard deviation, and relative standard deviation were listed in Table 6.1

Table 6.1 Method detection limits of some VOCs using OLMEM monitoring system

Replicate #	Benzene (ppbv)	TCE (ppbv)	Toluene (ppbv)	Ethylbenzen (ppbv)
Run #1	2.28	3.23	2.17	2.99
Run #2	2.29	2.95	2.35	2.87
Run #3	2.17	2.37	2.12	3.12
Run #4	2.30	3.33	2.13	3.50
Run #5	2.31	2.76	2.36	3.15
Run #6	2.28	2.75	2.38	3.37
Run #7	2.15	3.14	2.02	3.50
Run #8	2.11	3.15	2.30	3.25
Avg.	2.24	2.96	2.23	3.23
sd	0.074	0.30	0.13	0.21
%RSD	3.3	10	6.2	6.5
MDL	0.22	0.90	0.39	0.63

The method detection limit and the sensitivity of the monitoring system depends on the operating parameters as well as the designs of the membrane module. It is also directly related to the frequency of microtrap injection. If the injection interval is increased, the microtrap accumulates sample for a larger period of time and the detection limit decreases consequently. Therefore the MDL can be further lowed by using more fibers in the membrane module and longer microtrap interval.

6.3.1.3 Stability and Precision: The long term stability is also considered to be an important factor for a monitoring device. The long term stability and precision were measured by continuously monitoring a gas standard which contained 1 ppm benzene along with potential combustion products such as H_2O, CO_2, CO, SO_2, etc. A total of one hundred and forty four injections were made and the system response as a function of time (injection number) is plotted in Figure 6.4. The relative standard deviation in peak area of those one hundred and forty four injections was 4 % indicating good precision in the membrane extraction as well as microtrap preconcentration injection.

6.3.2 Optimization of the Operating Parameters

In order to achieve high sensitivity and low detection limit for the OLMEM monitoring system, it is desirable to transport as much as possible of VOCs through the membrane in to the GC separation column. Since the selective permeation of a VOC through a polymer membrane is a diffusion and dissolution process, the operating parameters such as the feed side pressure, the sample flow rate, the temperature of the membrane module, and the moisture in the sample will seriously affect the permeation rates of the test organic

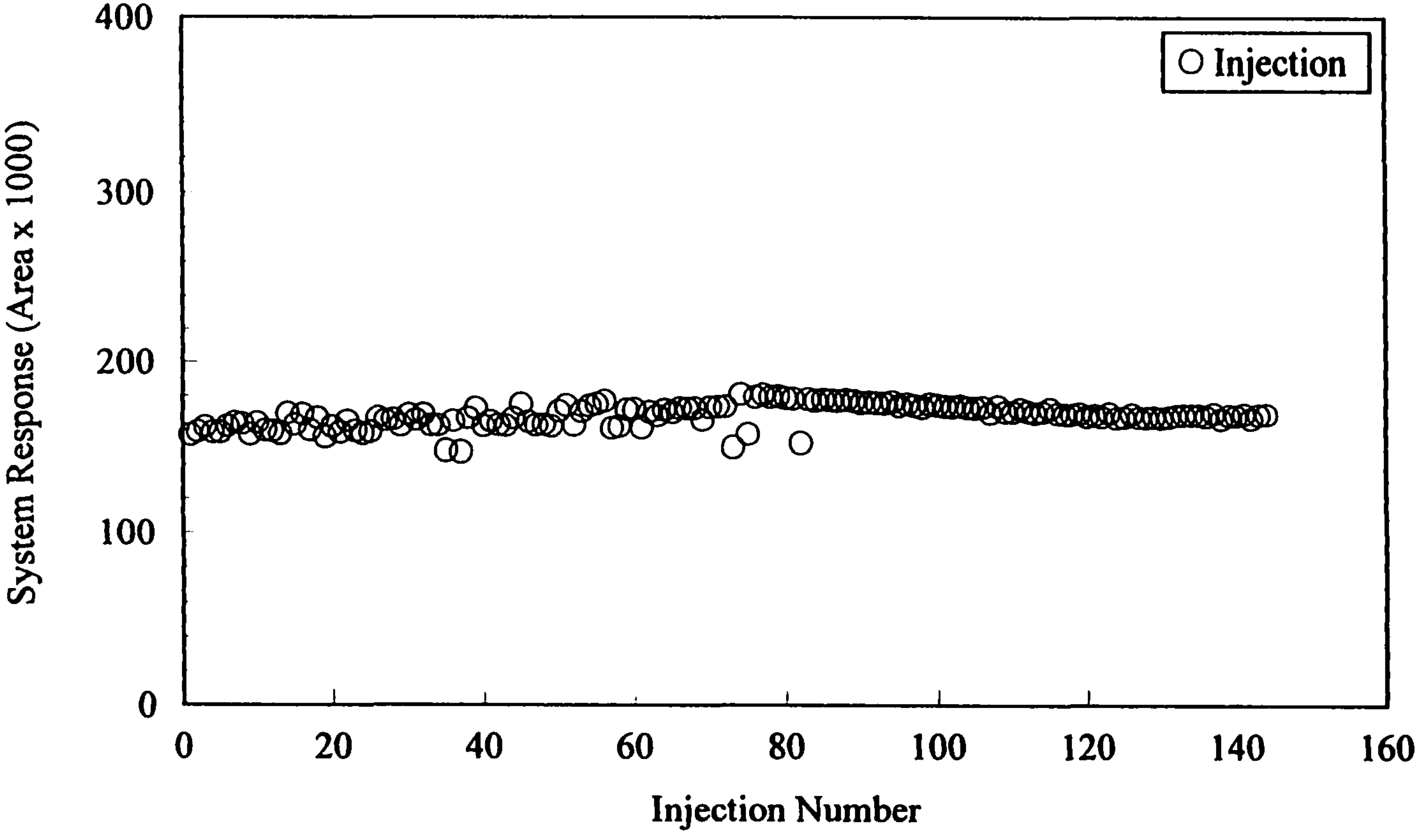


Figure 6.4 Reproducibility of the OLMEM monitoring system.

compounds and membrane extraction efficiency. The optimization of those operating parameters were investigated and are discussed in the following.

6.3.2.1 Effect of Pressure Differential: A permeation process can be spontaneous only if the chemical potential change of the permeant is negative. For a permeant/membrane system, the chemical potential change across the membrane from the feed side to the permeate side can be expressed as follows [Ho and Sirkar, (1992)]:

$$\mu_{ip} - \mu_{if} = RT * \ln\left(\frac{p_{ip}}{p_{if}}\right) \tag{6.2}$$

where, p_{ip} is the partial pressure of analyte i in the permeate side of membrane, and p_{if} is the partial pressure of i in the feed side. When the partial pressure of the feed side of the membrane is greater than the permeate side of the membrane, $p_{ip} < p_{if}$, $\ln\left(\frac{p_{ip}}{p_{if}}\right)$ negative, and the permeation process occurs spontaneously. In this case, the pressure difference (or the fugacity difference) offers the driving force needed for the mass transfer through the membrane. For a permeation process, the rate of permeation for a VOC through a membrane is dependent on its permeability P, the membrane thickness δ, and the partial pressure difference across the membrane according to the equation [Barrer, (1941)]:

$$\frac{q}{A} = \frac{(P * \Delta p)}{\delta} \tag{6.3}$$

where q is the flow rate of a permeant, A is membrane surface area; and Δp is the partial pressure differential of the permeant across the membrane. Hence for a given membrane

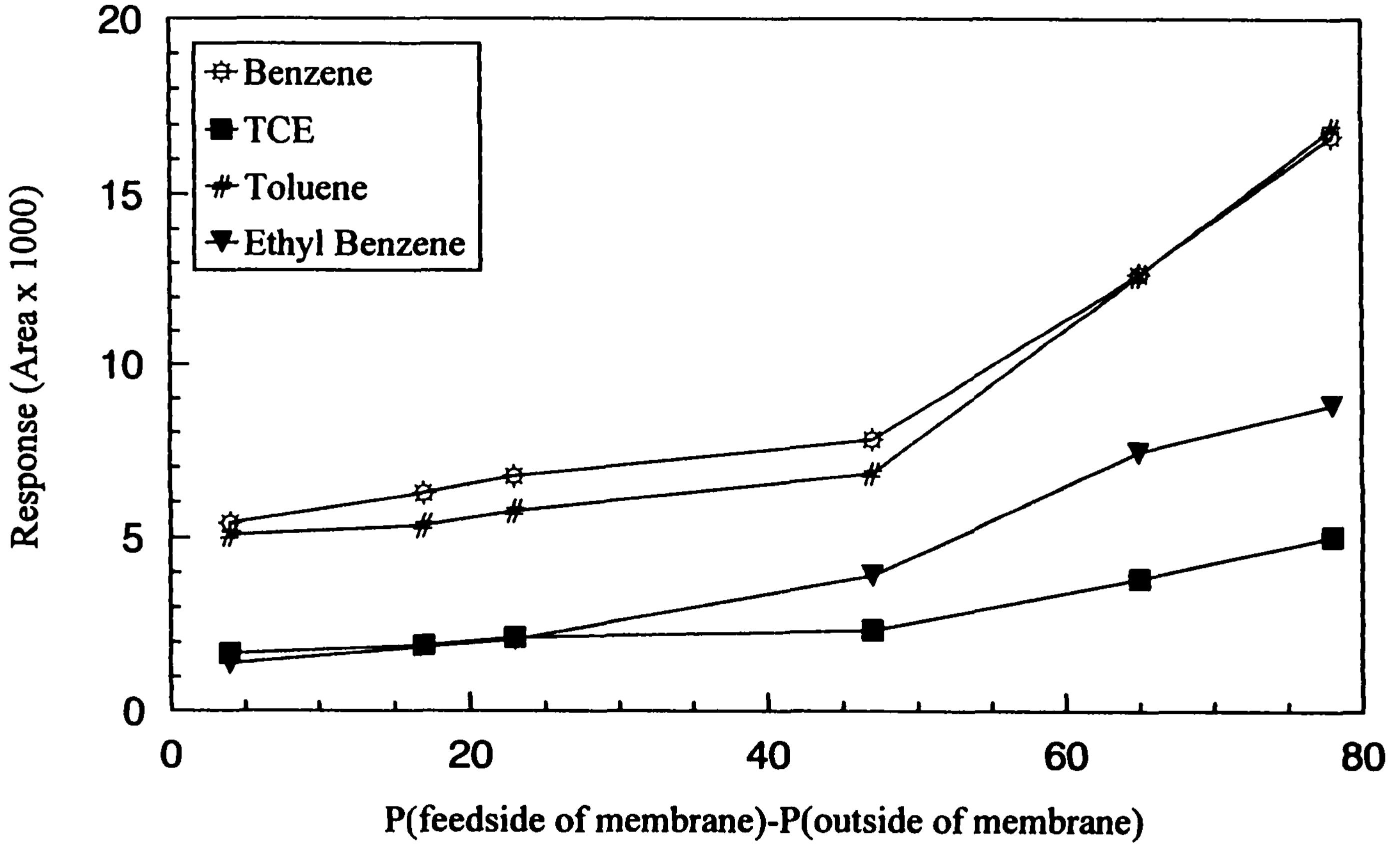


Figure 6.5 The effect of the pressure differential on the system response. The experiment was carred out at room temperature and sample flow rate was 30 ml/min.

module, the permeation of VOC through the membrane is proportional to the partial pressure differential.

The effect of the pressure differential on the response of the system was investigated. Experiments were done with Benzene, Toluene, TCE, and Ethylbenzene. The partial pressure gradient was provided by maintaining a pressure differential between the feed and permeate side of the membrane. N_2 was used as a stripping gas to carry away permeated VOCs continuously. In addition, the high pressure used in the feed side might have increased the sorption of VOC on the membrane structure and consequently raised the permeation flux. The results of the experiment are presented in Figure 6.5. It was observed that the response of the system increased with the increasing pressure differential between the feed and carrier gas side of membrane and the response increased sharply when the pressure difference was more than 45 psi. In this experimental system, the pressure in the permeate side of the membrane usually can not be very low because positive pressure is needed in a gas chromatography to push the sample through the analytical column. On the other hand, the silicone membranes are relatively delicate and are unable to withstand elevated pressures on the feed side. Therefore, the key to efficient operations is maintaining a optimal pressure differential without jeopardizing GC operation or destroying the membrane.

6.3.2.2 Effect of Sample Flow Rate on System Response and Extraction Efficiency:

Flow rate is an important parameter that determines system response. The effect of varying the flow rate of the air stream on the system response is shown in Figure 6.6 and 6.7. In the investigation, two kinds of membrane: silicone rubber and a composite

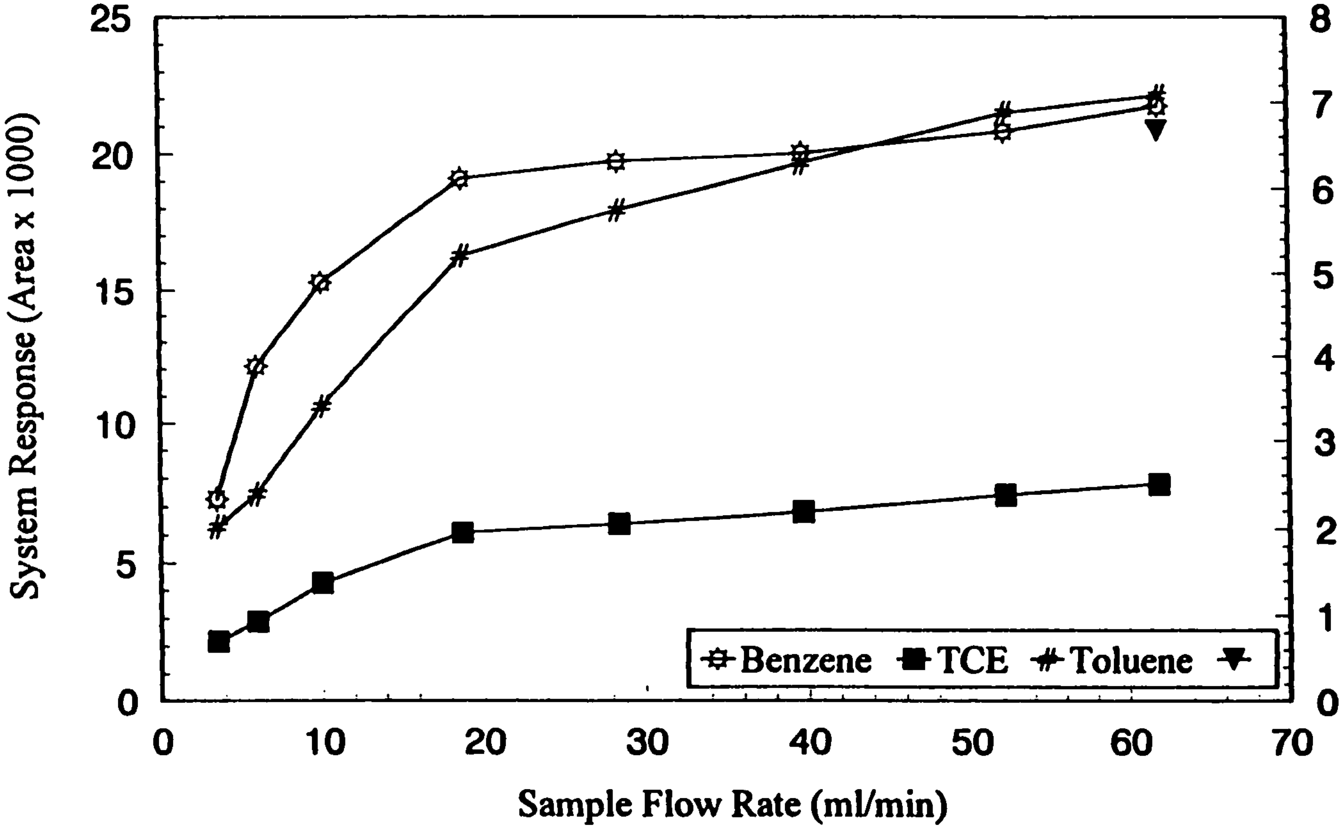


Figure 6.6 The effect of the sample flow rate on the system response. The single silicone rubber fiber module was used.

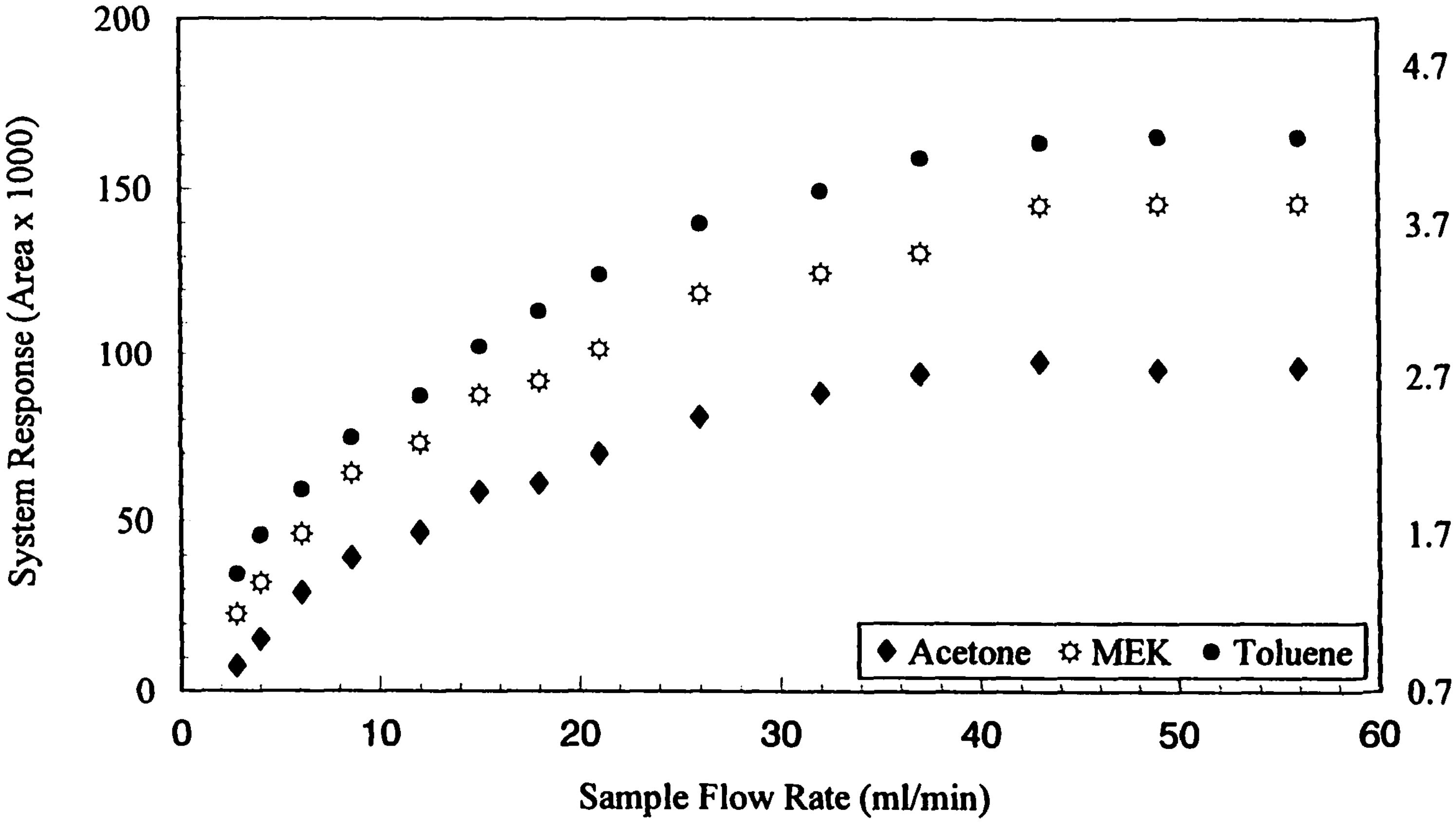


Figure 6.7 Effect of the sample flow rate on the system response. The single composite membrane module was used.

membrane were used. From the experimental results, it was observed that as the flow rate increased, the response of the system for both membranes increased till it reached a maximum point beyond which the response stayed constant. This result can be explained as follows. The resistance to mass transfer in the membrane permeation process occurs at three steps. First is the migration of VOCs to the membrane surface through a boundary layer. Second is the diffusion of VOCs through the membrane and third is the diffusion into the inert gas on the other side of the membrane. At low flow rates, the diffusion through the boundary layer may be the rate limiting step. But when the flow rate was increased, more turbulence was introduced destroying or reducing the boundary layer and increasing the total flux through the membrane. Consequently, the system response increased. However, when the flow rate was increased beyond a certain point, the response of the system did not increase any further because the rate controlling step was the diffusion through the membrane. This effect was more obviously observed for silicone rubber because it was a thicker film than the composite membrane in which top lay only 1 µm. Moreover, high flow rate reduced the residence time and consequently extraction efficiency. To balance these two opposing mechanisms the response finally reaches a constant value.

It must be noted that the flow rate experiment was carried out at a constant feed pressure. The combined effects of pressure differential and the flow rate differences on the response of the monitoring system are presented in Figure 6.8.

The extraction efficiency is another key parameter necessary for evaluating an extraction method. Extraction efficiency was measured by continuously monitoring a gas

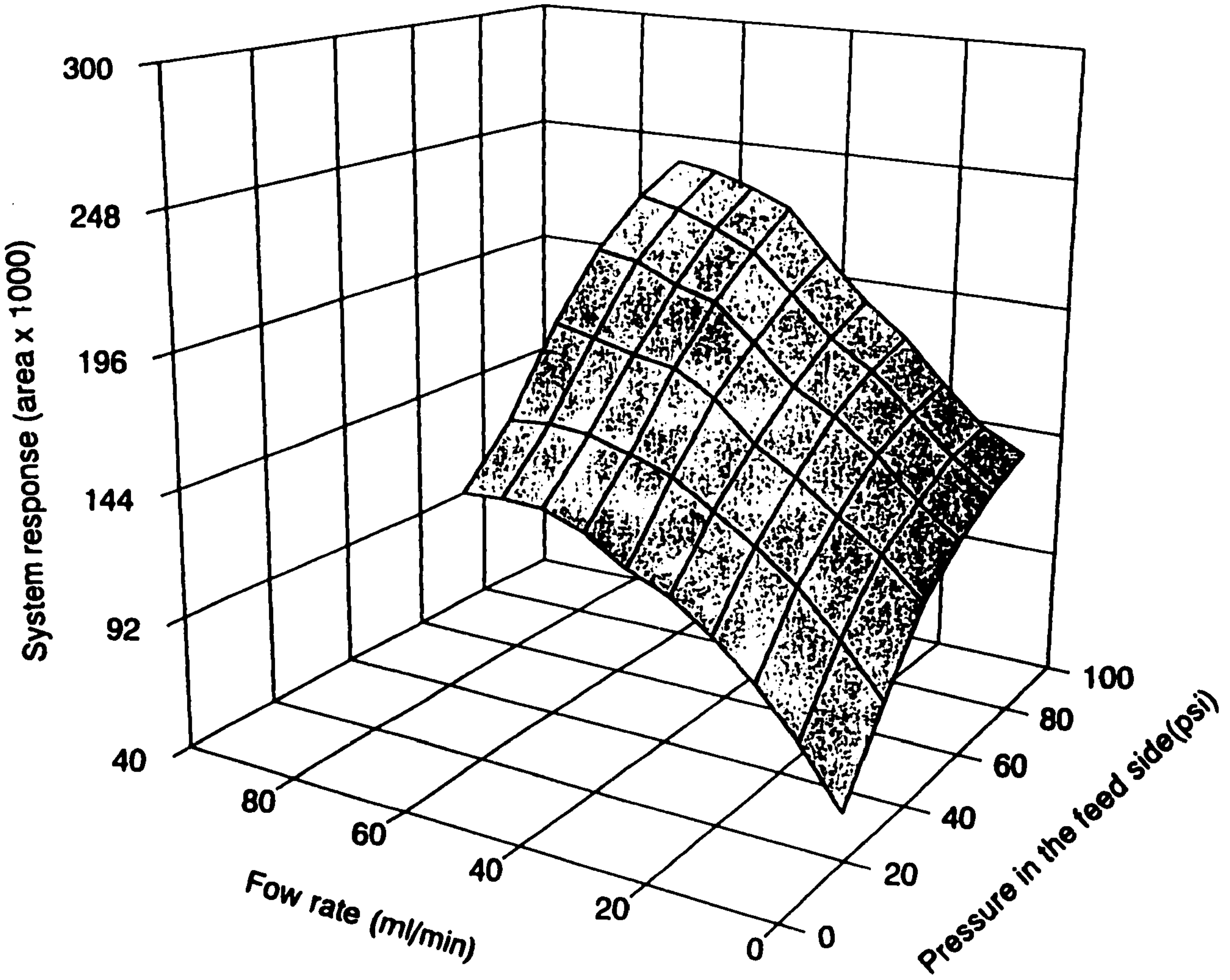


Figure 6.8 System response as a function of sample flow rate and feed pressure.

sample at the flow rate 10 ml/min, feed pressure 75 psi, and room temperature. The experimental data is listed in Table 6.2.

Table 6.2 The membrane extraction efficiency for tested VOCs

Compound	Concentration (ppm_v)	Extraction Recovery %
Acetone	4.6	76
Toluene	1.6	97
Methyl Ethyl Ketone	1.9	95

The investigation demonstrated that high extraction recovery could obtained using this monitoring system. The membrane module designs allow the simultaneous extraction and stripping of VOCs. The continuous stripping eliminates the equilibrium limitation and increases the extraction efficiency.

The extraction efficiency as a function of flow rate was also investigated and presented in Figure 6.9. The experiment was carried out at the feed pressure 55 psi using 1 ppmv of each benzene, TCE, toluene, and ethylbenzene, respectively. From Figure 6.9, it is seen that when flow rate was increased the extraction efficiency decreased although the system response increased. Higher flow rate brought a larger quantity of the analyte into the membrane module resulting in an increased mass flow through the membrane. However, high flow rates also resulted in shorter residence time leaving less time for permeation. So, beyond a certain flow rate, there was no net improvement in the system response.

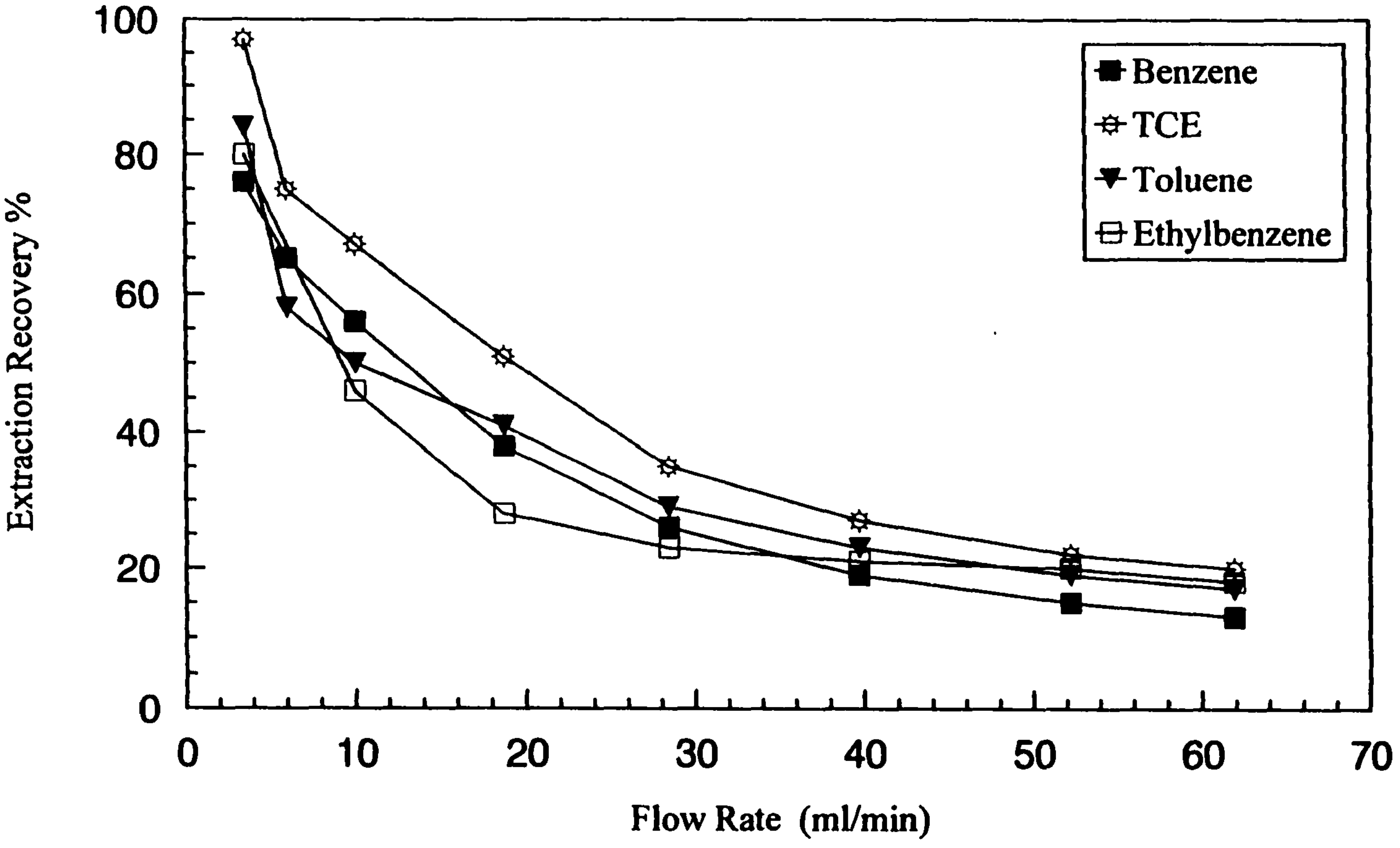


Figure 6.9 Extraction recovery as a function of the sample flow rates. The single silicone fiber module was used and the experiment was carried at room temperature.

6.3.2.3 The Effect of Temperature: The temperature of the sample flowing over the membrane and/or the temperature of a membrane module will affect the permeation rate of the VOCs and the air matrix. For the practical considerations, the effect of the temperature of the membrane module on the system response was investigated at a constant feed pressure and the results are shown in Figure 6.10. It was observed that at first the responses increased with the increase in temperature. Beyond a temperature of approximately 75 ^{0}C, the responses decreased with increase in temperature. This result is consistent with a mechanism in which the decrease in permeability of organic molecules occurs is due to their reduced partitioning into the membrane at higher temperatures.

The effect of temperature on the rate of permeation is dependent on the nature of the permeant. The studies conducted by Barre and other investigators [Barrer, Barrie, and Ranam, (1962); Suwandi and Stern, (1973)] showed that the permeability of silicone membrane for small, non-polar molecules decreases with increasing temperature due to decreasing solubility. For larger molecules with larger energies of activation, the permeability increases with increase in temperature. The permeability of analytes through the membrane is a product of diffusion and solubility coefficient. The diffusion coefficient increases with increasing temperature and obeys an Arrhenius type equation [Ho and Sirkar, (1992)]:

$$D = D_0 * \exp\left(\frac{E_d}{RT}\right) \tag{6.4}$$

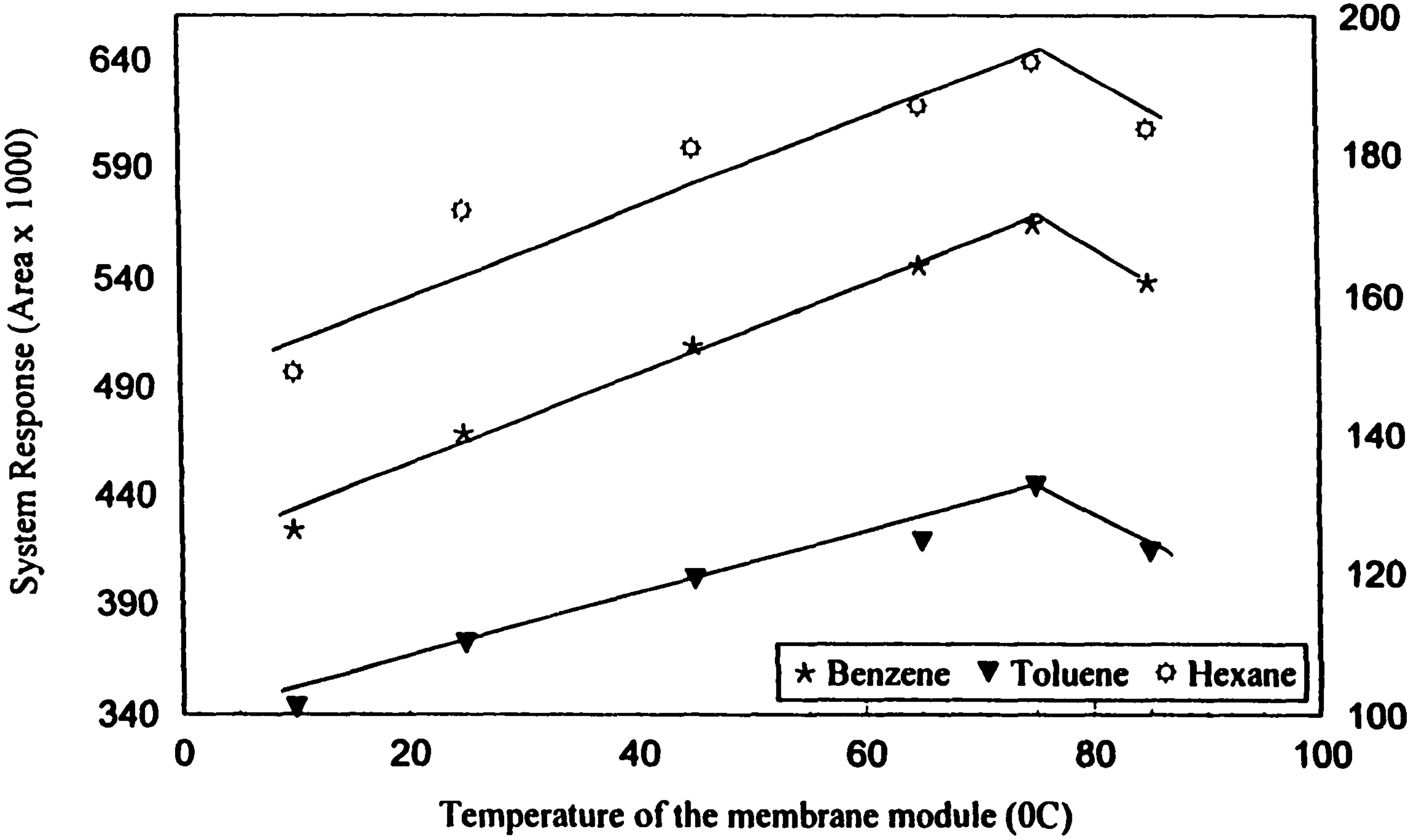


Figure 6.10 Effect of the temperature on OLMEM monitoring system response.

where E_d is the activation energy. Increasing the temperature of the membrane raises the response due to the increased rate of diffusion. On the other hand, the solubility of VOCs in silicone membrane decreases with increase in temperature:

$$S = S_0 * \exp\left(\frac{\Delta H}{RT}\right) \tag{6.5}$$

where ΔH is the enthalpy of sorption, which has a negative value for most organic compounds. Thus, the solubility of VOC in the polymer membrane decreases with increasing temperature. At higher temperatures, the decrease in solubility dominates and consequently the response of the system decreases.

Moreover, further increasing the temperature may reduce the lifetime or damage a membrane material. At a test temperature of 95 ^{0}C, the membrane module began to leak. The temperature limits for membranes are related to the glass transition temperature of the polymer, at which, the polymer chains become more mobile and the membrane is increasingly susceptible to creep and compaction.

6.3.2.4 Effect of Moisture on Membrane Permeation: The experiments were performed with humidified samples containing between 0.6 to 47% moisture. The results are presented in Figure 6.11. The amount of moisture added is significantly higher than what is normally encountered in ambient air samples although stack samples may have such high moisture content. Even at these high moisture contents, the system response did not show any appreciable change.

Permeation is a function of the chemical properties of both the permeant and the membrane. The chemical composition of the membrane substrate plays an important role.

The silicone membrane used in this study was hydrophobic and highly permeable to organic compounds. So the moisture did not effect the permeation of organic molecules. However, if condensation occurs on the membrane surface, the water layer may form a barrier to mass transfer and the system response may decrease. In this experiment, the membrane module was maintained at about 70 ^{0}C to prevent condensation. Moreover, the permeation process was carried out at a relatively high pressure and flow rate which further reduced the possibility of a boundary layer formation. The experiment demonstrated that the moisture content of the air sample did not limit the application of the on-line membrane extraction for VOCs monitoring. So, here membrane extraction acts a water management device by separating water from VOCs. This is very useful for air analysis because moisture has always been a problem in trace VOCs analysis.

6.4 Summary

The study has demonstrated that the on-line membrane extraction microtrap GC system can be used to provide continuous, real time (or near real time) monitoring of VOCs in air emissions at low ppb level. The monitoring system exhibited high sensitivity, good reproducibility and large linear dynamic range. In this monitoring system, the membrane acts as a separator. Simultaneous extraction and stripping of VOCs takes place in a single step. Consequently, the extraction efficiency is fairly high. The microtrap not only serves as a preconcentrator but also an automatic injector. Another advantage of this system is its ability to handle samples with high moisture content. The investigations also show that optimization of operating conditions was necessary for obtaining good results.

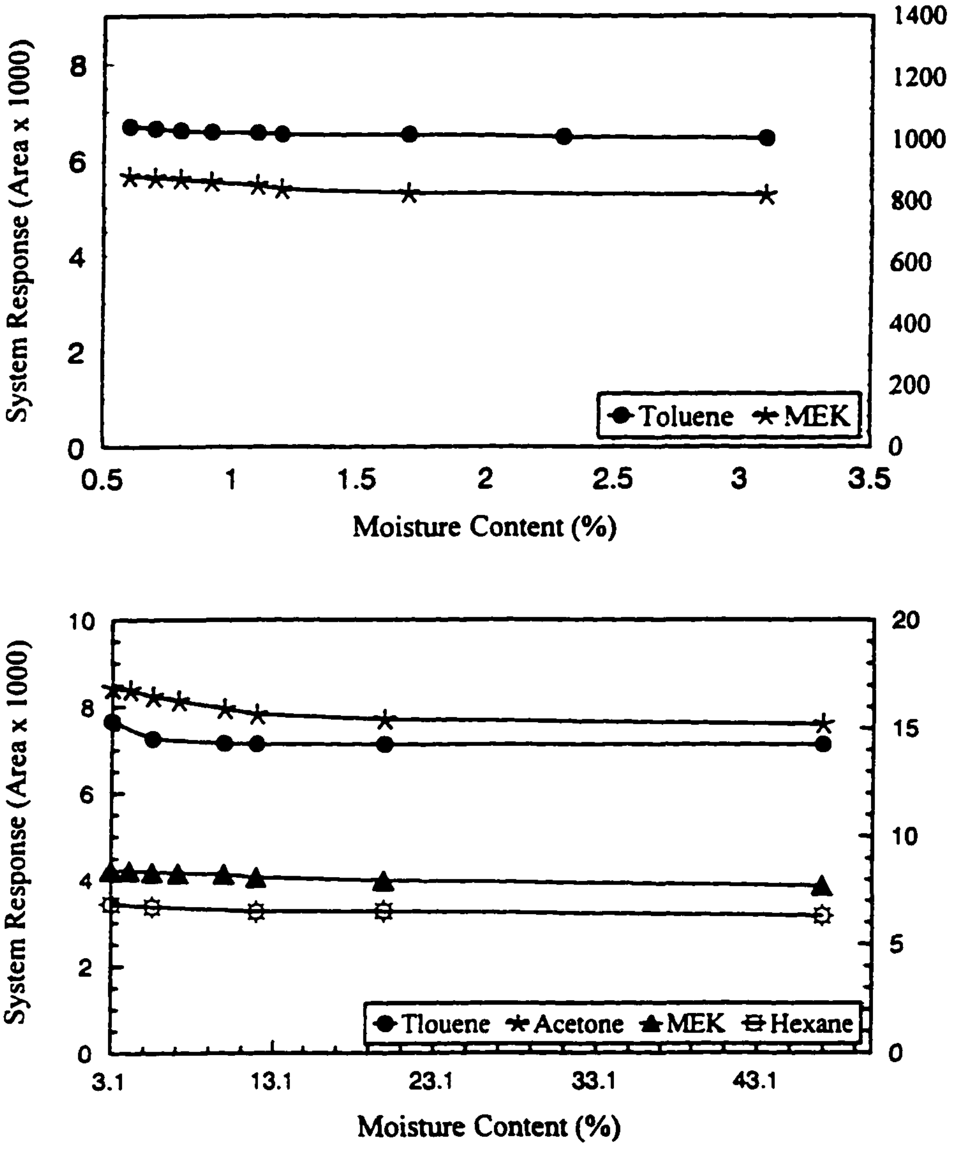


Figure 6.11 Effect of moisture in air sample on system response. The feed pressure was 60 psi and the flow rate was 30 ml/min.

CHAPTER 7

ON-LINE MEMBRANE EXTRACTION MICROTRAP GC SYSTEM FOR CONTINUOUS MONITORING OF VOCs IN AIR EMISSION

(PART II: APPLICATION AND RESPONSE CHARACTERISTICS)

7.1 Introduction

In the previous chapter the advantages of the On-line Membrane Extraction Microtrap (OLMEM) system in air monitoring have been demonstrated. The OLMEM system is able to monitor VOCs at low ppb levels and can handle complex environmental samples with high moisture content. Studies have shown that membrane extraction of VOCs from complex air emissions is particularly attractive in continuous monitoring applications because the air steam can continuously flow through or over the membrane. The VOCs can selectively permeate through the membrane while the bulk matrix of air as well as other interferences are reduced. The permeated VOCs can be entrained by an inert gas such as nitrogen and then transported to an analytical column.

In this chapter, the applicability of the OLMEM system in a real-world application is demonstrated by monitoring the emissions from an air toxic control device. Emissions containing VOCs and toxic gaseous compounds can be controlled by many techniques such as carbon adsorption, condensing system, wet scrubbing, biodegradation, membrane separation, and incineration. However, the preferred method for VOC emission control is incineration, in which VOCs are converted to carbon dioxide and water by burning at temperatures grater than 1000 ^{0}C (conventional thermal incineration) or catalytic oxidation at relative low temperatures normally ranging from 300 to 400 ^{0}C [Glassman, (1997); Yu, (1996)]. Compared to thermal incineration, the catalytic incineration provides lower operating temperature, less toxic products, and more flexibility.

In this approach, a laboratory scale catalytic incinerator is set up and the emissions are monitored using the OLMEM system. The characteristics of the catalytic incinerator such as the conversion efficiency, reproducibility, response time, and the effect of the concentration variations of VOC are investigated.

Membrane extraction of VOCs is a complex process. The nature of the membrane and permeant, as well as the system operation parameters will seriously affect the permeation rate and separation of VOC from the air matrix. Some of the important operation parameters were investigated in the previous study.

Response characteristics of a membrane permeator is another important factor for continuous monitoring techniques because the purpose of installing a on-line monitoring system is to obtain the information on a time scale that is comparable to concentration changes in the process. There is always a certain amount of dead volume associated with plumbing through which the sample is transferred from the process to the analyzer. This always contributes to a lag or delay time in response. In addition, for a membrane based monitoring system, the time taken by VOCs to permeate through the membrane is an important factor.

To see what effect the membrane had on increasing the time lag, the response characteristics for both OLMEM system and OLMEM-Incinerator system are investigated in this further study.

7.2 Experimental Section

The experimental system consisted of a catalytic incinerator, a membrane module, a microtrap, and a GC/FID. This is shown in Figure 7.1. The gas samples containing VOCs continuously flowed into the catalytic incinerator. The emission at the outlet which contained large quantities of H_2O, combustion products, and trace levels of unconverted VOCs passed into the membrane module containing one or more hollow fibers. Nitrogen (stripping gas) flowed countercurrently around the membrane fibers and carried permeated VOCs to the microtrap where VOCs were trapped. The microtrap was placed at the entrance to the GC column and sample was introduced directly into the column through the microtrap. Here, the microtrap served the dual purpose of preconcentration and injection for continuous monitoring of VOCs. The microtrap was heated by passing a pulse of electrical current directly through the tube wall. The microtrap injections were made at regular intervals (every 20 sec. to 4 min.), and corresponding to each injection, a chromatogram was obtained (Figure 7.2).

All analyses were performed using a GC (Model 5890, Hewlett Packard Inc., Avondale, PA) equipped with a flame ionization detector. A 30 m long, 0.53 mm I.D., and 3 μm thick film DB-624 column (J&W Scientific, Folsom, CA, USA) was used for separation. The data acquisition and analysis were done using HP 3365 Chemstation. The organic compounds used to make standards were reagent grade chemicals from Fisher Scientific. Certified gas standard from ALPHGAZ Inc. (Morrisville, PA, USA) was used for quantitation. The microtrap was made by packing a 0.53 mm I.D. deactivated fused-silica lined stainless steel tubing with commercial absorbent, Carbotrap™ C (Supelco Inc., Supelco Park, PA). The length of the microtrap was about 15 cm. The membrane

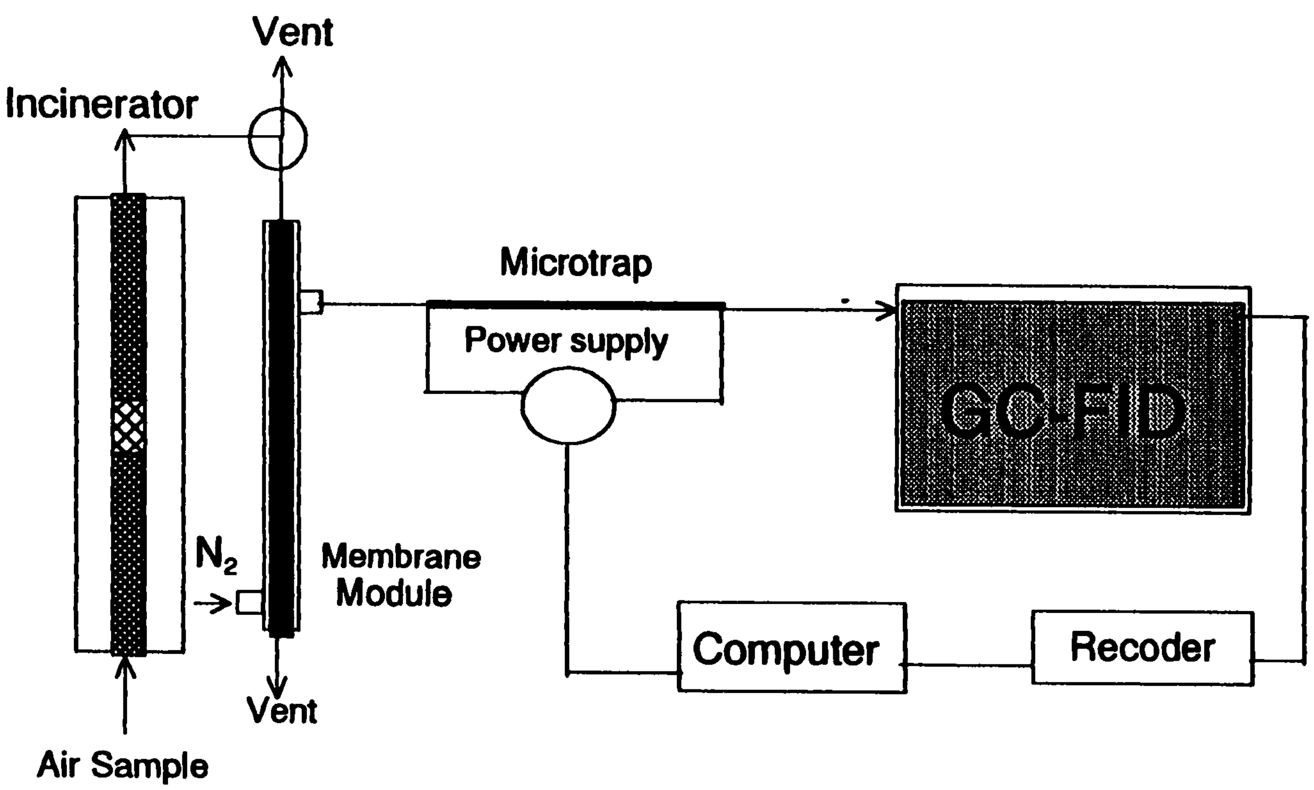


Figure 7.1 On-line membrane extraction microtrap–GC system.

module was constructed with as many as twenty 6 inch long membrane fibers. A microporous polypropylene hollow fiber coated with 1μm thick film of homogenous silicone (Applied Membrane Technology, Minnetranka, MN) was used in this study. The fibers were 0.260 mm O.D. and 0.206 mm I.D. A laboratory scale catalytic incinerator was set up which generated the VOC emissions. The catalytic reactor was a 2.5 cm O.D. stainless tubular reactor placed in a temperature controlled horizontal furnace. (Lindberg, Watertown, WI, USA). The catalyst (Engelhard Corporation, Edison, NJ) was 1.5% platinum deposited on an Y-alumina washcoat and carried on a 400 (or 200) cells per square inch cordierite honeycomb. The length of catalyst bed was 0.5 cm.

7.3 Results and Discussion

7.3.1 Evaluation of the Catalytic Incinerator

A laboratory scale catalytic incinerator was selected in this study to destroy the VOCs in a simulated gas stream containing acetone, benzene, and toluene. Platinum was selected as a catalyst because of its high activity. During the incineration process, the OLMEM system was connected to the incinerator for continuous on-line monitoring of emissions. The gas stream containing VOCs flowed continuously through the catalytic incinerator. The emission at the outlet of the incinerator passed into the membrane module. The microtrap pulses were made at the fixed intervals of time, and the chromatogram of the three compounds corresponding to each injection was obtained. Figure 7.2 demonstrates continuous monitoring of acetone, benzene and toluene at the outlet of the reactor. In about 2 hours of continuous monitoring, a total of twenty-eight consecutive microtrap injections were made and the relative standard deviations of peak area for acetone,

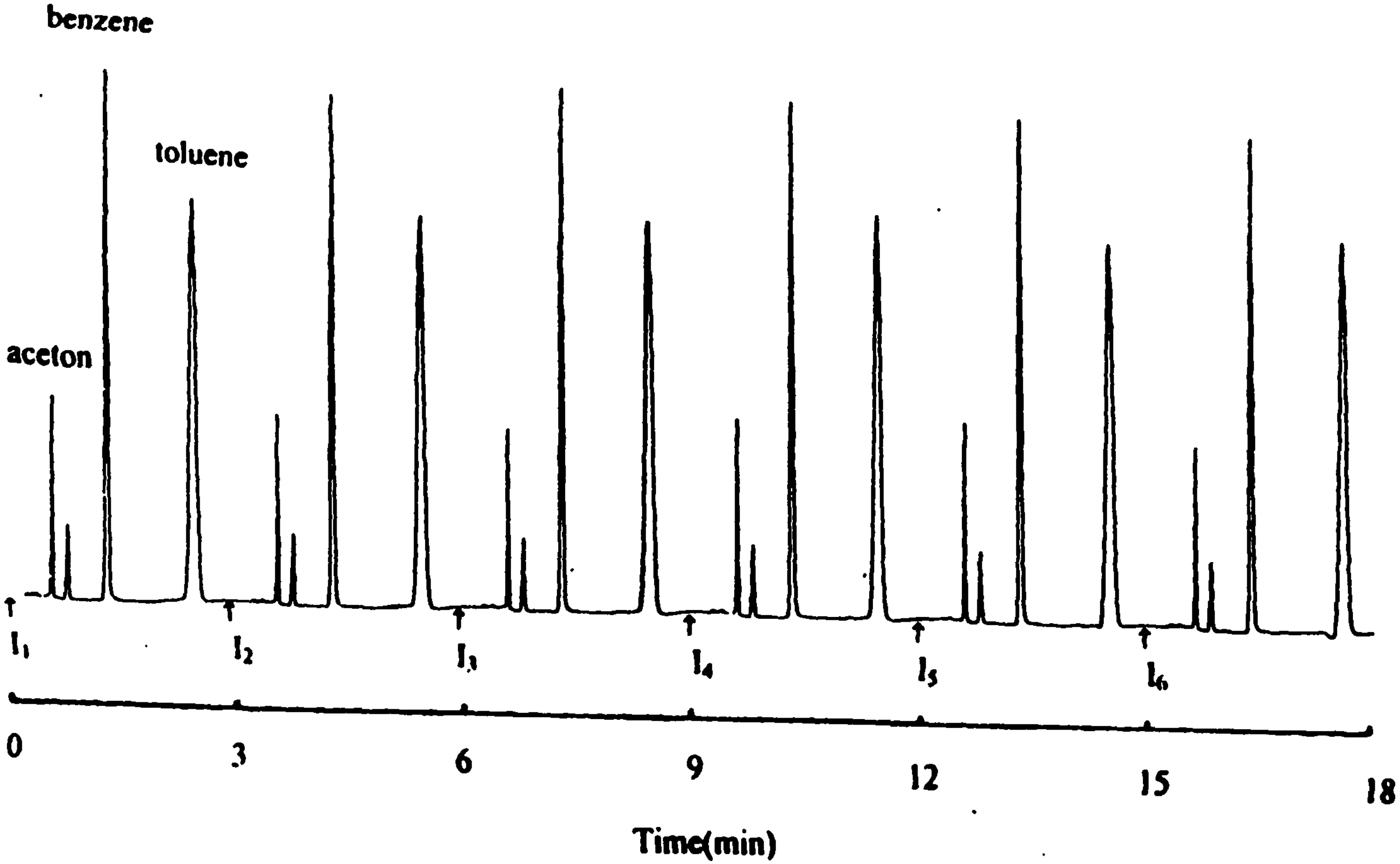


Figure 7.2 Continuous monitoring of benzene, toluene, and acetone at the oulet of the catalytic incinerator. I1, I2, I3......are the injection corresponding to which chromatograms are obtained

benzene, and toluene were 6.34%, 5.36%, and 5.84% respectively. The results show that the incineration process was stable and also monitoring system had good reproducibility.

The OLMEM system was useful in evaluating the performance of the catalytic incinerator. For example, destruction efficiency expressed as percentage conversion:

$$\%Conversion = \left[1 - \left(\frac{outlet\ concentration}{inlet\ concentration}\right)\right] * 100 \qquad (7.1)$$

is an important parameter which is a measure of what percentage of VOCs are destroyed. Conversion depends upon temperature of the catalyst bed because the catalytic activity increases with increasing temperature. The effect of the incineration temperature on the conversion of VOCs was investigated and presented in Figure 7.3 & 7.4. Here the outlet concentration is plotted as a function of the temperature of the catalyst bed. At high conversion, even if inlet concentration is high, the outlet concentration can be quite low. For example if inlet concentration is 1 ppm, at 99% destruction efficiency the outlet concentration would be only 10 ppb. Such low concentration can not be measured by a conventional on-line analyzer. Figure 7.2 demonstrates the capability of the OLMEM system to monitor low ppb level VOCs at the outlet of the incinerator. From Figure 7.3, it is observed that the conversion increased with increasing the operating temperature of the catalytic incinerator. When the incinerator temperature reached 400 ^{0}C, the conversion was as high as 99.94% for benzene, 99.78% for toluene, and 99.84% for acetone.

For a gas-solid catalytic reaction, the overall reaction basically can be divided to following several steps [Glassman, (1977); Yu, (1996)]. First, VOC molecules transfer to the external surface of a catalyst from bulk air and then diffuse through the pores to the internal catalytic surface through the pores in the catalyst. Next, the VOCs are adsorbed

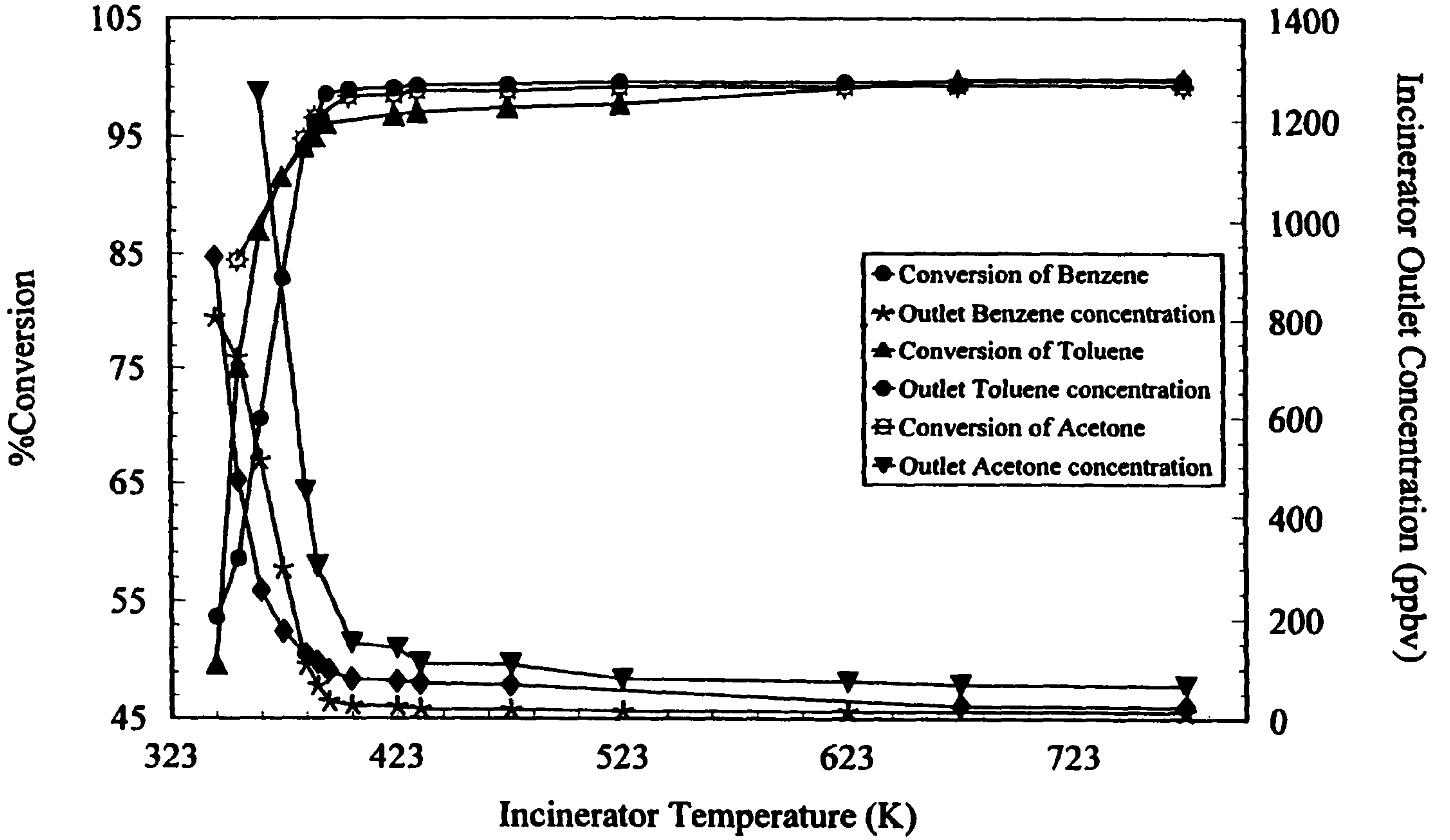


Figure 7.3 Conversion and outlet concentration as function of the incinerator temperature. Inlet concentrations of VOCs were 1.7 ppmv of Benzene, 1.8 ppmv of Toluene, and 8.6 ppmv Acetone, respectively.

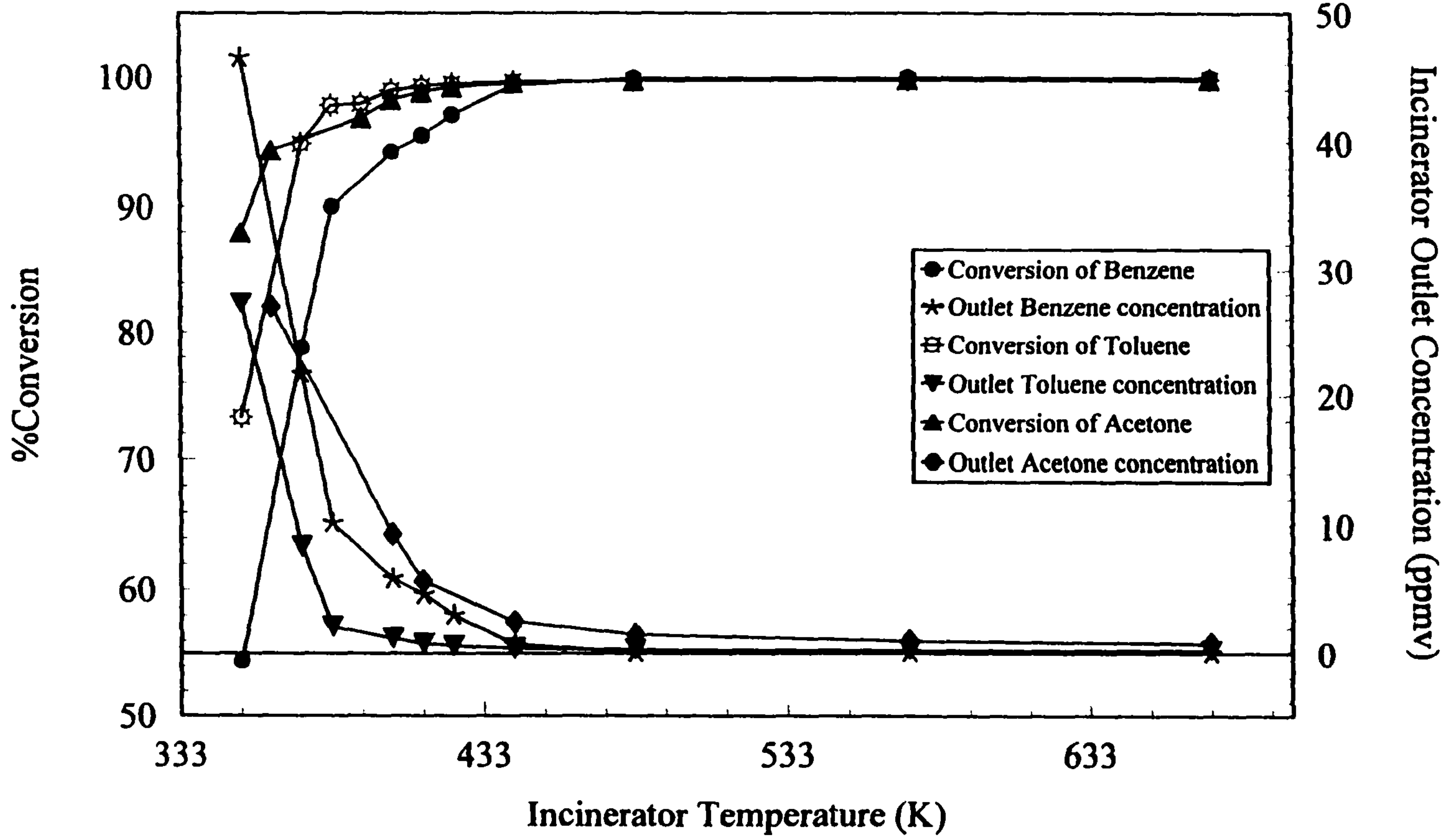
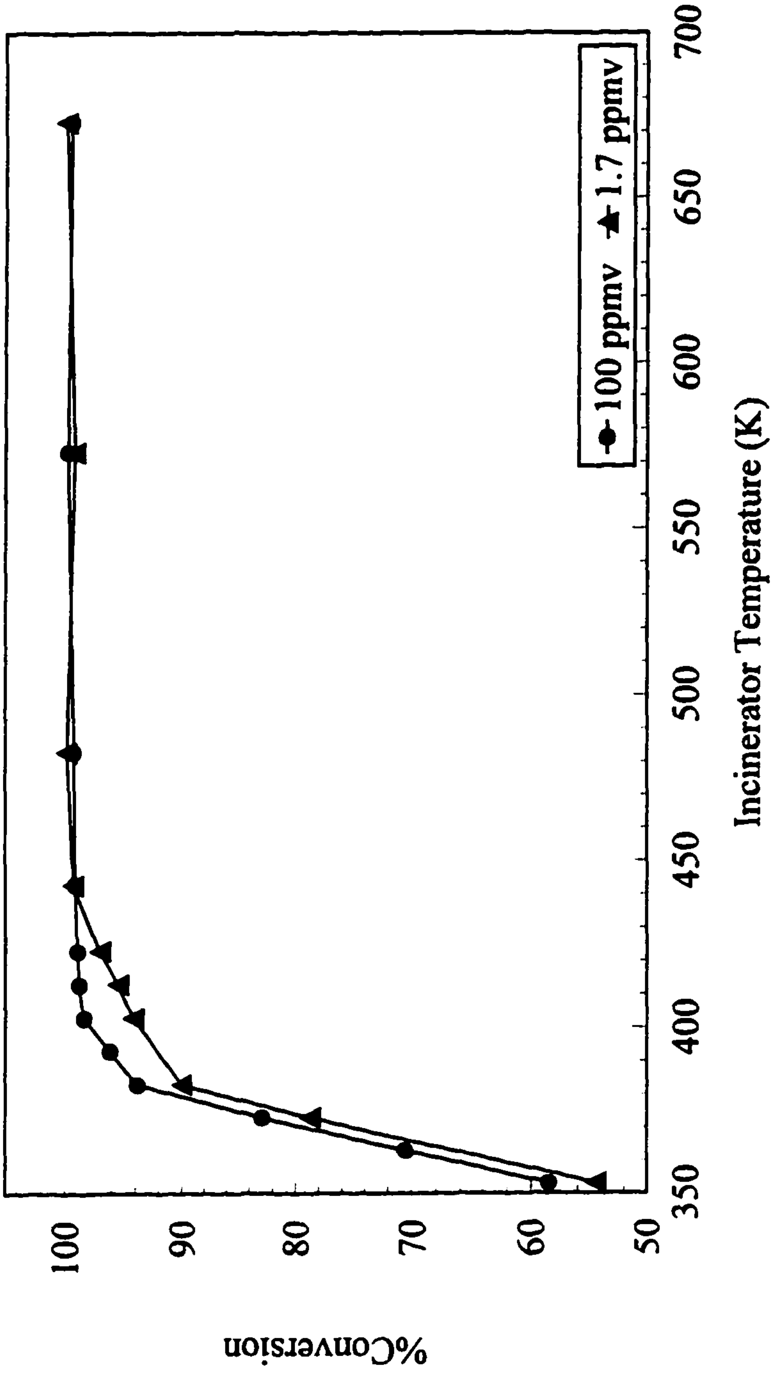


Figure 7.4 Conversion and outlet concentration as function of the incinerator temperature. Inlet concentrtions were 100 ppmv of Benzene, Toluene, and Acetone, respectively.

and the reaction occurs on the catalyst surface. Then, the products desorb and diffuse from the pore structure to the external surface. Finally, the products transfer from the external catalyst surface to the bulk gas. The experimental results presented in the Figure 7.3 & 7.4 illustrate that the conversions of acetone, benzene, and toluene followed the three stages mentioned above: mass transfer, pore diffusion, and kinetic control. In Figure 7.3 & 7.4, the rising portion of the curve was kinetically controlled and was dependent upon temperature. Eventually, conversion became independent of temperature because now the process was limited by mass transfer. These results are in agreement with known theory of catalytic oxidation.

The effect of inlet concentration difference of VOC on the conversion percentage was also investigated. Figure 7.5 is a plot of conversion as function of temperature at two different concentrations. Here two different concentrations 102.7 ppm and 1.2 ppm were tried and the results were almost identical, demonstrating that conversion was independent of inlet concentration. This is also in agreement with theory. For example, for an arbitrary reaction: A + B ⇒ D. When [B] >>[A], the reaction could be treated as first order reaction (pseudo-first order) [Glasman, (1977)]. Therefore, the concentration at a certain time A is given as: $[A] = [A_0]K$, where $[A_0]$ is initial concentration (here, the inlet concentration) and K is a constant. For such a reaction, the conversion could be expressed as:

$$\begin{aligned} \%Conversion &= \left(1 - \frac{outlet\ concentration}{inlet\ concentration}\right) * 100 \\ &= \left\{1 - \frac{[A_0] * K}{[A_0]}\right\} * 100 = (1 - K) * 100 \end{aligned} \qquad (7.2)$$



Fiure 7.5 The effect of the incinerator outlet concentration change on the %Conversion of Benzene

Thus, conversion is not a function of the inlet concentration. In this experiment, the catalytic oxidation process can be treated as pseudo-first order reaction since the concentration of O_2 in the gas stream is much greater than the concentration of VOCs. Results in Figure 7.3 and 7.4 demonstrate the use of the OLMEM system for studying reaction kinetics.

7.3.2 Response Characteristics

Response time of the analytical system is an important parameter in continuous monitoring applications. The important factor here is the time taken by a sample molecule to diffuse through the membrane which results in a delay before the system responds to a change in concentration.

The response time of the OLMEM monitoring system was studied by injecting a few microliters of the sample vapor into an air stream entering the membrane module. Then, the test compound in the strip gas was monitored by pulsing the microtrap every 10 seconds. There is considerable amount of dead volume in the membrane module and the associated plumbing. This also accounts for a certain time delay. An injection of the same quantity of the sample through the module with the membrane removed served as a blank. Hexane, 1,2-dichloroethane (DCE), methanol (MEOH), and methyl ethyl ketone (MEK) were used in this test.

The experimental results are listed in the Table 7.1. The response profiles for hexane and DCE are presented in Figure 7.6 and for oxygenated compounds: methanol and MEK in Figure 7.7.

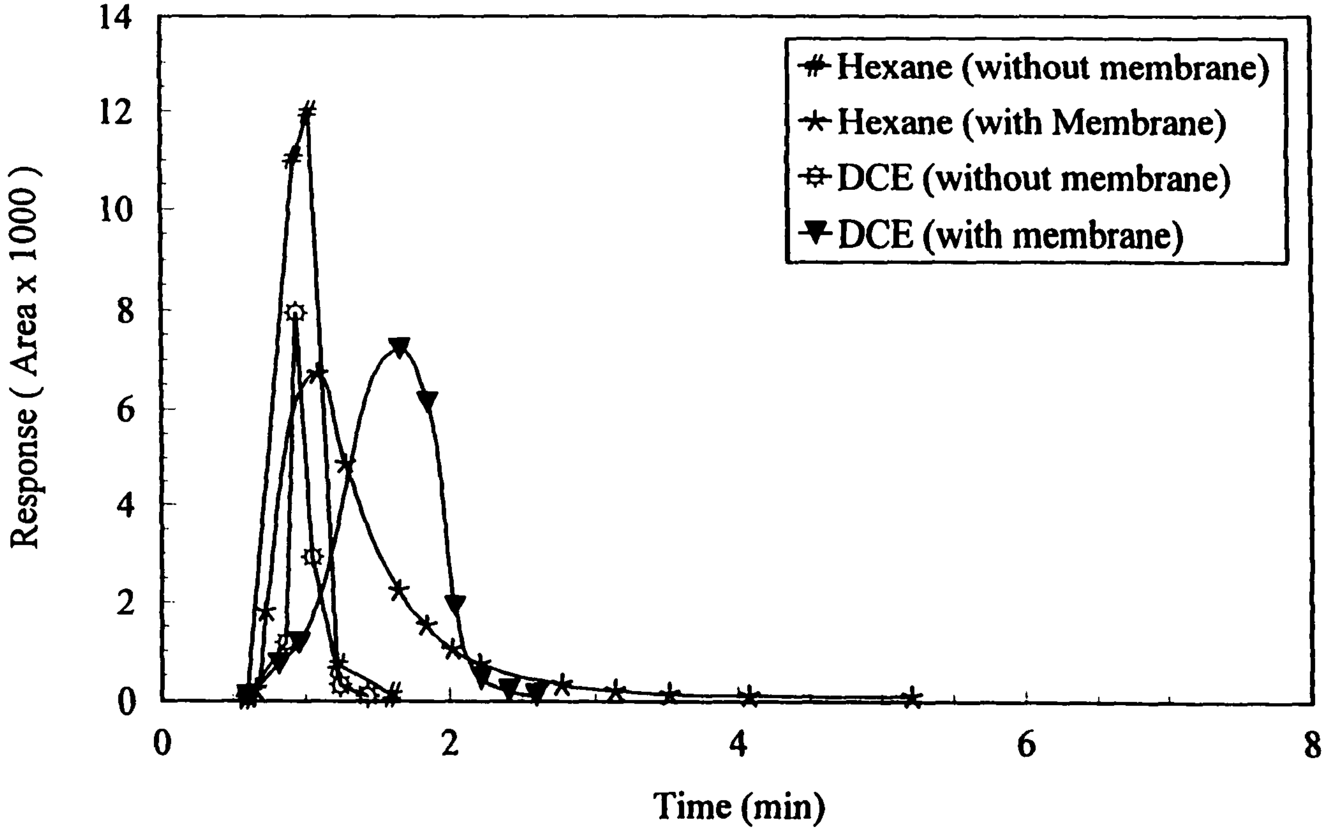


Figure 7.6 The response profiles for hexane and DCE using OLMEM monitoring system

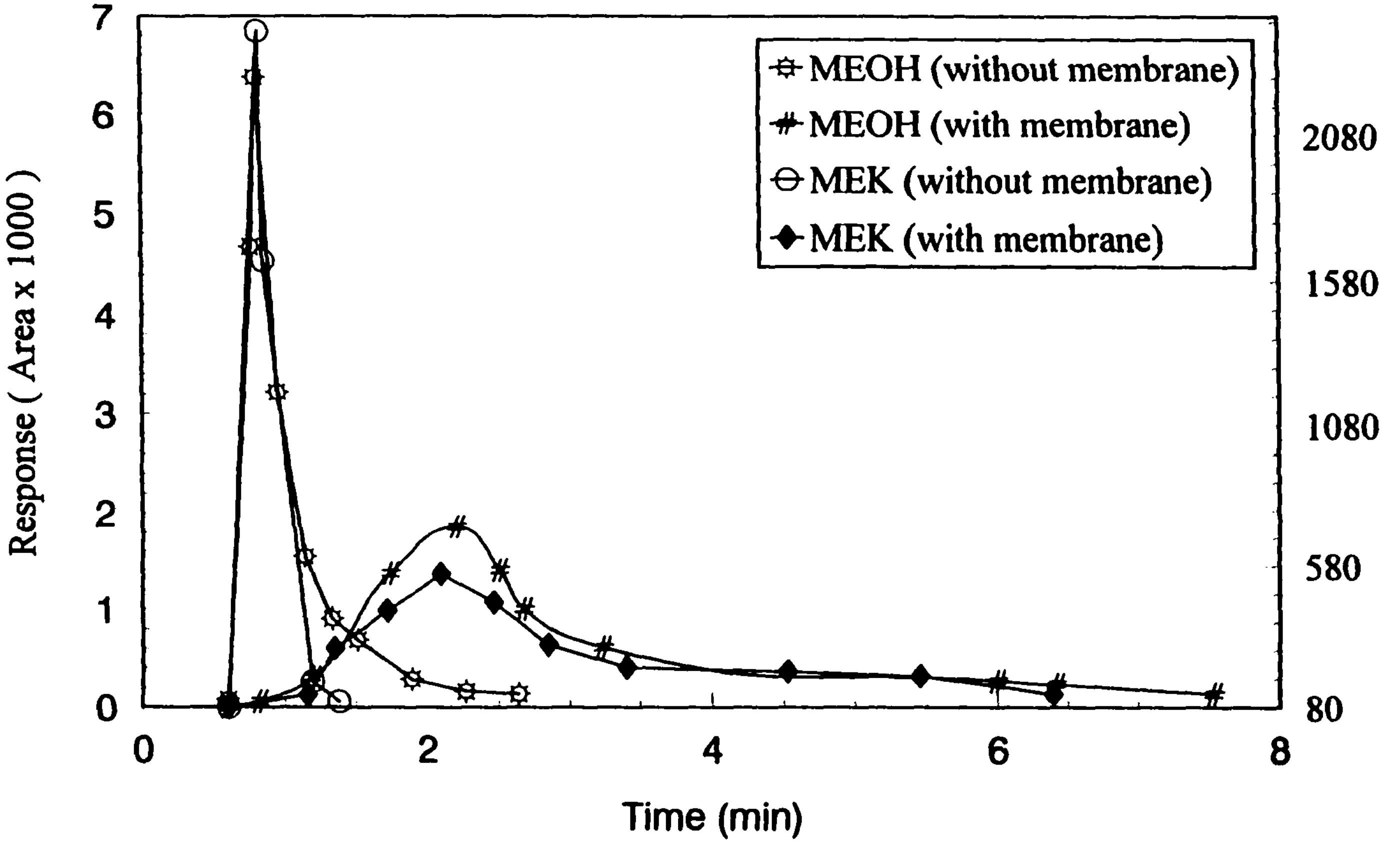


Figure 7.7 The response profiles for oxygenated compounds: Methanol (MEOH) and MEK using OLMEM monitoring system

Table 7.1 Response time of different compounds

Compound	T_{max} (min)	T_{blank} (min)	DTL = T_{max}-T_{blank} (min)
Hexane	1.09	0.93	0.16
DCE	1.66	0.94	0.72
MEK	2.10	0.82	1.28
MEOH	2.12	0.80	1.32

T_{max}: Time at which maximum response occurs.

T_{blank}: Time of maximum response in the blank module.

The lag time is defined as the interval between the time the gas comes in contact with the membrane until it emerges on the other side [Frisch, (1957)]. Tailoring that definition to this system, considering dissolution and diffusion effects, a differential time lag (DTL) is defined as the difference between T_{max} and T_{blank}. In Table 7.1, it is observed that the value of T_{blank} was very similar for all the compounds. The value of DTL depends upon the compound and can vary any where between 0.16 to 1.32 min. The DTL decreased in the following order: MEOH > MEK > DCE > Hexane.

The study demonstrated that a quick response to concentration change is possible using this monitoring system. The fast response may be attributed to using a composite membrane. A permeance, P'_c, of a VOC in a composite membrane is related to the permeance, P'_s, of the microporous polypropylene support and the permeance, P'_f, in silicone film:

$$\frac{1}{P'_c} = \frac{1}{P'_s} + \frac{1}{P'_f} \tag{7.3}$$

Since the polypropylene support membrane is a porous material and the permeation of VOCs through such membrane is much faster than in silicon film, the equation 7.4 can be expressed as follows:

$$\frac{1}{P'_c} = \frac{1}{P'_f} \tag{7.4}$$

that is, the permeance of the composite membrane can be represented by the permeance of the silicon film covering the support material surface. The permeance is a measure of the flux which is inversely proportional to the membrane thickness. When using a thinner silicon film, the permeance will increase and the response time will decrease. Consequently, the VOCs will more quickly permeate though the membrane. A study conducted by other investigators shows that doubling the membrane thickness results in an increase in response time by a factor of 4 [Kotiaho, et al. (1991)]. Therefore, the membrane thickness is a vital parameter in the membrane based monitoring device and the thinner film is preferred for quick system response.

The calculation of the absolute lag time is complicated because the diffusion process depends upon several factors. If the diffusion coefficient of the analyte is constant, the lag time, L_t, can be calculated using the following simple expression [Frisch, (1957)]:

$$L_t = \frac{\delta^2}{6D_0} \tag{7.5}$$

where D_0 is the diffusion coefficient of the gas, and δ is the thickness of the membrane. For a certain compound D_0 depends upon concentration, the type of membrane, temperature, cross-linking and chemical nature of the polymer, the structure and polarity of the diffusing molecule. So, in real situations where the diffusion coefficient can not be assumed to be constant, lag time calculation results in very complex relations [Siegel, (1986)].

Size of the molecule is an important factor; smaller molecules tend to diffuse faster than larger molecules. But for partitioning in the membrane, size of the molecule as well as polarity are important factors. Larger molecules adsorb more strongly than smaller ones. Non-polar molecules tend to dissolve faster than polar compounds in the non-polar silicone membranes. Here, the DTL for the non-polar hexane was smaller than DCE which is slightly polar, and is much smaller than MEK which is even more polar. Polarity is undoubtedly a major factor affecting the DTL. On the other hand, although the polarity of MEOH is approximately one half that of MEK (dipole moment of methanol is 1.7 D) as compared to 3.3 D for MEK [Reid, Prusnitz, and Poling, (1987)], the DTLs were approximately the same. This suggests that the functional group was also a significant factor. The size of the molecule was not a factor here because MEK is larger than MEOH. If size and polarity were the only factors, then, the DTL of MEK should have been considerably larger than that of MEOH. So it is concluded that the functional group also plays an important role, here the hydroxyl group appears to contribute to a higher DTL than the carbonyl group. Furthermore, the polarities of DCE and MEOH are approximately the same (the dipole moment for DCE is 1.8 D). Nevertheless, the DTL for DCE was approximately one half of that for MEOH. Here again the higher DTL is attributed to the hydroxyl group.

The response time for OLMEM-Incinerator system was also measured in this study by the procedure mentioned below, and the response profile is presented in Figure 7.8. With the catalyst bed maintained at a high temperature, 150 ppm Benzene was continuously introduced into the incinerator for 1 minute. The emission from the incinerator outlet passed through the OLMEM system and analyzed by GC. It can be seen that the OLMEM system responded within 30 second after the introduction of the sample. Within two minutes of sample introduction, the response already reached its maximum value. In the previous study using only OLMEM system, the experimental results demonstrated that the lag time can vary anywhere between a few seconds to one or two minutes. Here the OLMEM system response lasted for almost eight minuets after the concentration impulse was removed. This was mainly due to the large internal volume of the catalytic reactor and large amount of tubing and plumbing associated with it.

To see what effect the membrane had on increasing the lag, an analysis was also done with the reactor system as it is, but with the membrane removed. This served as a blank for the dead volume in the associated plumbing. A profile similar to the one showed in Figure 7.8 was obtained. The peak maxima occurred 43 seconds earlier when the membrane was removed. So it may be assumed that the delay in response that may be attributed to membrane permeation is about 43 seconds. Compared to insitu spectroscopic probes such as FTIR, this may be a long delay, but for an extractive sampling system this is relatively low. The delay due to the dead volume appears to be more significant. When used in a large field unit, the plumbing would be larger and more delay may be expected.

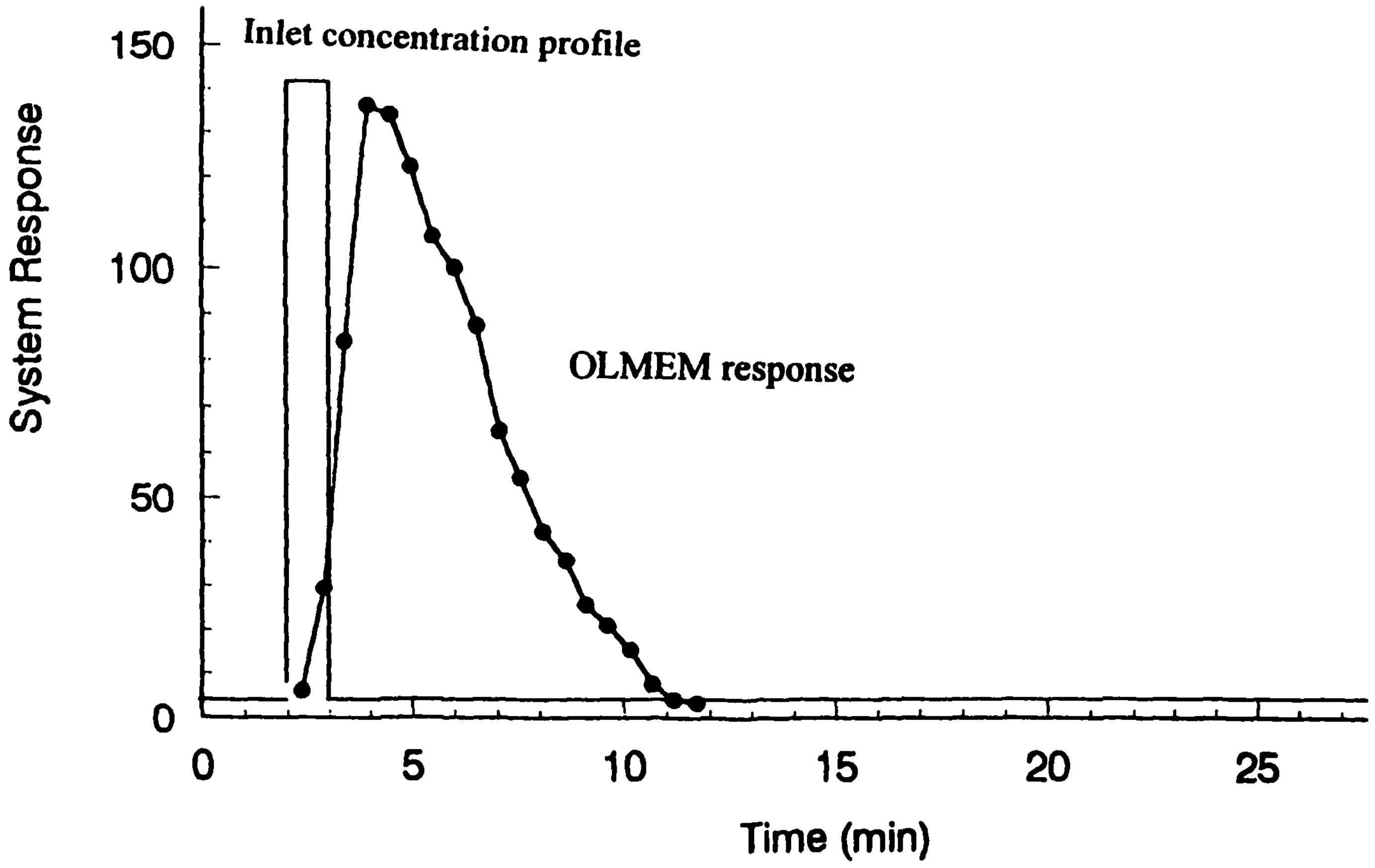


Figure 7.8 The response profiles for OLMEM-Incinerator system.

7.4 Summary

This investigation further demonstrated that the OLMEM system is able to continuously monitor VOCs emissions even at low ppb level from an emission source such as a catalytic incinerator, which usually is unable detected by a conventional monitoring method. In the OLMEM system, simultaneous extraction and stripping of VOCs takes place in a single step and nitrogen is used as a stripping gas to remove the equilibrium limitation at the membrane surface. This single-step sample preparation ensures good precision and simplicity and allows easy automation and on-site operation. Because both the membrane extraction module and microtrap interface include no moving parts, the monitoring system can be rugged and suitable for long-term field application.

In summation, the advantages of the OLMEM system include high sensitivity, time efficiency, quick response (response time at the order of 60 to 90 sec.), simplicity, low cost, elimination of solvents and other sample preparation steps, durability, and easy automation. The analytical system can be used to study, optimize, and potentially to help control and automate processes.

Other applications of the OLMEM system are possible. For example, the system can be modified using a pump and a sampling valve to monitor indoor and/or outdoor ambient air. In addition, the OLMEM can be installed in a portable instrument, which is attached to an exhaust system of an automobile for continuous monitoring of the engine performance. This technique may also be applied in a remote sensing station that is capable of collecting analysis data continuously without any human intervention.

CHAPTER 8

CONCLUSION

In this study, two novel techniques, based on membrane permeation, for sampling and analysis of trace level volatile organic compounds from air were developed.

The advantages of sampling with hollow fiber membranes include the ability of the membrane to provide efficient extraction of organic compounds from air and elimination of interference such as water, the simplicity of the membrane extractor device, the high sample surface area-to-volume ratio in the hollow fiber, the ability to obtain high linear flows at relatively low sample flow rate, low cost, durability, and easy automation.

The MPCS system demonstrated that both non-polar and polar volatile organic compounds existing at trace levels in air can be preconcentrated by membrane permeation. Another advantage of this sampling system is that it eliminates water from the air sample and the membrane permeator acts as a water management device. A passive sampling system that incorporates a permeator design which uses the vacuum in the canister to draw a concentrated sample into the canister appeared to function quite effectively. The VMMGC analytical system can be used to analyze the trace VOCs in a low pressure canister.

The OLMEM monitoring system demonstrated that this system can be used to provide continuous, real or near real time monitoring of VOCs in air emissions at low ppb level. The monitoring system exhibited high sensitivity, good reproducibility, large linear dynamic range, and response times on the order of 60 to 90 sec. In this system, the membrane acts as a separator. Simultaneous extraction and stripping of VOCs takes place in a single step. The microtrap not only serves as a preconcentrator but also an automatic injector. Because both the membrane extraction module and microtrap interface include no moving parts, the monitoring system can be rugged and suitable for long-term field applications. Another advantage of this system is its ability to handle samples with high moisture content.

Moreover, both studies show that the optimization of operating conditions such as pressure difference, sample flow rate, temperature, sampling time, membrane material and film thickness, etc. is necessary for obtaining good results.

Furthermore, both studies show that these two systems can be used to study the permeation mechanism of VOCs at trace concentration and can provide data to refine the theoretical models needed to propel more sophisticated membrane applications at trace levels.

However, to establish membrane permeation based sampling and analysis systems as a leading technique for trace level VOCs analysis, further developments are required in the membrane technology. Upon the availability of membrane materials with different or improved selectivities, a wider range of organic compounds can be efficiently collected and analyzed using those two methods.

REFERENCES

Akard, Michael and Richard K. Sacks, "High-Speed GC Air Monitor Using Cryointegration for Sample Collection.". *J. of Chromatogr Sci.*, vol. 32, pp. 499-505, 1994.

Atkins, Peter, *Physical Chemistry.* fifth ed. W. H. Freman and Company, New York, NY, 1994.

Bai, Chuanshen, Meng-Dong Jia, John L. Falconer, and Richard D. Noble, "Preparation and Sepration of Silicalite Composite Membranes." *J. of Membrane Sci.*, vol. 105, pp. 79-87, 1995.

Baker Richard W. and Johannes G. Wijmans, "Membrane Separation of Organic Vapors from Gas Streams." In: D. R. Paul (eds.), *Polymeric Gas Separation Membranes*, CRC Press, Inc., Boca Raton, FL, pp. 353-397, 1994.

Baker, Richard W., Noriaki Yoshioka, Judith M. Mohr, and Amy J. Khan, "Separation of Organic Vapors from Air." *J. of Membrane Sci.*, vol. 31(213), pp. 259-272, 1987.

Barrer, R. M., *Diffusion In and Through Solids*. Cambridge University Press, Cambridge, MA, 1941.

Bauer Scott J. and R. Graham Cooks, "MIMS for Trace-level Determination of Organic Analytes in On-line Process Monitoring and Environmental Analysis." *American Laboratory*, pp. 36-51, 1993.

Beckman, Igor N., "Unusual Membrane Processes: Non-Steady-State Regimes, Nonhomogeneous and Moving Membranes." In: D. R. Paul (eds.), *Polymeric Gas Separation Membranes*, CRC Press, Inc., Boca Raton, FL, pp. 302-351, 1994.

Blume, I., P. J. F. Schwering, M. H. V. Mulder, and C. A. Smolders, "Vapor Sorption and Permeation Properties of Poly (dimethylsiloxane) Films." *J. of Membrane Sci.*, vol. 61, pp. 85-97, 1991.

Chiu, Chen-Hwa, "Advances in Gas Separation." *Hydrocarbon Processing*, pp. 69-70, January 1990.

Crank, J. and G. Park, *Diffusion in Polymers*. Academic Press, London, 1968.

Erb, J., E. Ortiz, and G. Woodside, "On-line Characterization of Stack Emissions." *Chemical Engineering Process*, pp. 40-45, 1990.

Favre E., P. Schaetzel, Q. T. Nguygen, R. Clement, and J. Neel, "Sorption, Diffusion and Vapor Permeation of Various Penetrants Through Dense Poly (dimethylsiloxane) membranes: a Transport Analysis." *J. of Membrane Sci.*, vol. 92, pp. 169-184, 1994.

Feng, X., S. Sourirajan, H. Tegel and T. Matsuura, "Separation of Organic Vapor from Air by Aromatic Polyimide Membranes." *J. Appl. Polym. Sci.*, vol. 43, pp. 1071-1079, 1991.

Fleming, G. K., "Dilation of Silicone Rubber and Glassy Polycarbonate Due To High Pressure Gas Sorption." Ph.D. dissertation. University of Texas at Austin, TX, 1987.

Fritsch, D., K. V. Peinemann, and R. D. Behling, "Silicone/non-silicone Grafted Blend Composite Membrane for Air/vapor Separation." *Desalination*, vol. 90, pp. 235-247, 1993.

Fujita, H., "Organic Vapors above the Glass Transition Temperature." In J. Crank and G. B. Park (Eds.), *Diffusion in Polymers*, Academic, New York, NY, pp. 75-105, 1968.

Geankoplis, Christie J., *Transport Processes and Unit Operations*. Allyn and Bacon, Inc., Boston, MA, pp. 302-307, 1978.

Ghosh, A. C., S. Borthakur, N. N. Dutta, "Adsorption of Carbon Monoxide in Hollow Fiber Membranes." *J. of Membrane Sci.*, vol. 96, pp. 183-192, 1994.

Giannovario, J., R. Grob, and P. Rulon, "Analysis of Trace pollutants in the Air by Means of Cryogenic Gas Chromatography." *J. Chromatogr.*, vol. 121, pp. 285-294, 1976.

Glassman, Irvin, *Combustion*. Academic Press, Inc. New York, NY, 1977.

Hamm, S. and P. Warneck, "Gas Chromatographic Determination of Acetonitrile in Air Using a Thermionic Detector." *Anal. Chem.*, vol. 62, pp. 1876-1883, 1990.

Hancock, J., J. McAndless, and R. Hicken, "A Solid Adsorbent Based System for the Sampling and Analysis of Organic Compounds in Air: An Application to Compounds of Chemical Defense Interest." *J. Chromatogr. Sci.*, vol. 29, pp. 40-45, 1991.

Harland, Brian J., Peter J. D. Nicholson, and Edward Gillings, "Determination of Volatile Organic Compounds in Aqueous Systems by Membrane Inlet Mass Spectrometry." *Wat. Res.*, Great Britain, vol. 21(1), pp. 107-113, 1987.

Ho, W. S. Winston and Kamalesh K. Sirkar,. *Membrane Handbook*. Van Nostrand Reinhold, NY, 1992.

Houde, A. Y., S. S. Kulkarni, U. K. Kharul, S. G. Charati, and M. G. Kulkarni, "Gas Permeation in Polyarylates: Effects of Polarity and Intersegmental Mobility." *J. of Membrane Sci.*, vol. 103, pp. 167-174, 1995.

Hsu, J. P., Greg Miller, and Victor Moran, III., "Analytical Method for Determination of Trace Organics in Gas Samples Collected by Canister." *J. of Chromatogr. Sci.*, vol. 29, pp. 83-88, 1991.

Ji, Wenchang, Subhas K. Sikdar, Sun-Tak Hwang, "Modeling of Multicomponent Pervaporation for Removal of Volatile Organic Compounds from Water." *J. of Membrane Sci.*, vol. 93, pp. 1-19, 1994.

Ji, Wenchang, A. Hilaly, Subhas K. Sikdar, and Sun-Tak Hwang, "Optimization of Multicomponent Pervaporation for Removal of Volatile Organic Compounds from Water." *J. of Membrane Sci.*, vol. 97, pp. 109-125, 1994.

Jonsson, J., J. Vojrosta, and J. Novak, "Systematic Errors Occurring With the Use of Gas-Sampling Loop Injectors in Gas Chromatography." *J. of Chromatogr.*, vol. 236, pp. 307-312, 1982.

Kesting, R. E., *Synthetic Polymeric Membrane*. 2nd ed., Wiley-Interscience, New York, NY, 1985.

Koros, W. J. and R. T. Chen, *Handbook of Separation Process Technology*. Wiley-Interscience, New York, NY, 1987.

Koros, W. J., *Gas Separation, in Membrane Separation Systems*. U.S. Dept. of Energy, Office of Energy Research, Report DOE/ER/30133-H1, vol. 2, pp. 1-50, 1990.

Kotiaho, Tapio, Frants R. Lauritsen, Tarun K. Choudhury, and R. Graham Cooks, "Membrane Introduction Mass Spectrometry." *Anal. Chem.*, vol. 63(18), pp.875A-883A, 1991

LaPack, M. A., James C. Tou, and Christie G. Enke, "Membrane Mass Spectrometry for the Direct Trace Analysis of Volatile Organic Compounds in Air and Water." *Anal. Chem.*, vol. 62(13), pp. 1265-1271, 1990.

LaPack, M. A. and James C. Tou, "Membrane Extraction Mass Spectrometry for the On-line Analysis of Gas and Liquid Process Streams." *Anal. Chem.*, vol. 68(15), pp. 1631-1337, 1991.

Lebovits, Alexander, "Permeability of Polymers to Gases, Vapors, and Liquids." *Modern Plastics*, pp. 139-205, March 1966.

Matson, S. L., J. Lopez, and J. A. Quinn, "Separation of Gases with Synthetic Membranes." *Chem. Eng. Sci.*, Great Britain, vol. 8(4), pp. 503-524, 1983.

McCabe, W. L., J. C. Smith, and P. Harriott, *Unit Operations of Chemical Engineering.* McGraw-Hill Book Company, New York, NY, 1985.

Meares, Patrick, *Membrane Separation Processes.* Elsevier Science Publishers, Oxford, OX, U.K., pp. 40-45, 1976.

Melcher, Richard G. and Paul L. Morabito, "Membrane/Gas Chromatographic System for Automated Extraction and Determination of Trace Organic in Aqueous Samples." *Anal. Chem.*, vol. 62(20), pp. 2183-2188, 1990.

Mitra, Somenath and Y. Chen, "Continuous Gas Chromatographic Monitoring of Low Concentration Sample Streams Using an On-line Microtrap." *J. Chromatogr.* Vol. 648, pp. 415-421, 1993.

Mitra, Somenath and Arthur Lai, "A Sequential Valve-Microtrap Injection System for Continuous, On-line Gas Chromatographic Analysis at Trace Levels." *J. of Chromatogr. Sci.*, vol. 33, pp. 285-289, 1995.

Mitra, Somenath, N. Zhu, X. Zhang, B. Kebbekus, "Continuous Monitoring of Volatile Organic Compounds in Air Emissions Using an On-line Extraction-Microtrap-Gas Chromatographic System." *J. Chromatogr.* A. vol. 736, pp. 165-173, 1996.

Mitra, Somenath, L. Zhang, N. Zhu, and X. Guo, "Characteristics of On-line Membrane Extraction Microtrap GC System as Applied to Air and Water Monitoring." *J. Microcolumn Separations*, vol. 8(1), pp. 21-27, 1996.

Mitra, Somenath, Y. H. Xu, W. Chen, and A. Lai,. "Characteristics of Microtrap-based Injection Systems for Continuous Monitoring of Volatile Organic Compounds by Gas Chromatography." *J. of Chromatogr.* A. vol. 727, pp. 111-118, 1996.

Moder, M., *Basic Principles of Membrane Technology.* Kluwer Academic Publishers, Norwell, MA, 1991.

Nguyen, Q. T., J. L. Ninow, and I. Mare, *Modeling of the Behaviour of Microporous Membrane Sensors Used in the Detection of Volatile Organic Solutes in Aqueous Media.* Elsevier Science Publishers, Oxford, OX, U.K., 1991.

Patil, G. S., M. Bora, and N. N. Dutta, "Empirical Correlations for Prediction of Permeability of Gases/Liquids Through Polymers." *J. of Membrane Sci.*, vol. 101, pp. 145-152, 1995.

Paul, D. R. and Yu. P. Yampol'skii, *Polymeric Gas Separation Membranes.* CRC Press, Inc., Boca Raton, FL, pp. 1-15, 1994.

Pebler A., "Gas Sampling System for Use in Hostile Environments." *Anal. Chem.*, vol. 18(I), pp. 63-79, 1989.

Peinemann, Klaus-Viktor, Judith M. Mohr, and Richard W. Baker, "The separation of Organic Vapors from Air." *AICHE Symposium Series 250*, vol. 82, pp. 19-27, 1986

Petropoulos, J. H., "Mechanisms and Theories for Sorption and Diffusion of Gases in Polymers." In: D. R. Paul (eds.), *Polymeric Gas Separation Membranes*, CRC Press, Inc., Boca Raton, FL, pp. 17-82, 1994.

Plate, N. A., Ye. M. Antipov, V. V. Teplyakov, V. S. Khotimskii, and Yu, P. Yampol'skii, "Polysilicon Hydrocarbons: Synthesis, Structure and Gas Separating Properties: Review." *Polymer Science USSR*, vol. 32, pp. 1053-1068, 1990.

Prasad, R., R. L. Shaner, and K. J. Doshi, "Comparison of Membranes With Other Gas Separation." In: D. R. Paul (eds.), *Polymeric Gas Separation Membranes*, CRC Press, Inc., Boca Raton, FL, pp. 514-614, 1994.

Pratt, Katherine F. and Janusz Pawliszyn, "Gas Extraction Kinetics of Volatile Organic Species from Water with a Hollow Fiber Membrane." *Anal. Chem.*, vol. 64(18), pp. 2101-2106,

Pratt, Katherine F. and Janusz Pawliszyn, "Water Monitoring System Based on Gas Extraction with a Single Hollow Fiber Membrane and Gas Chromatographic Cryotrapping." *Anal. Chem.*, vol. 64(18), pp. 2107-2110, 1992.

Reid, R. C., J. M. Prausnitz, B. E. Poling,. *The Properties of Gases and Liquids.* McGraw-Hill, NY, 4th ed., 1987.

Rosa, M. J., and M. N. de Pinho, "Separation of Organic Solutes by Membrane Pressure-Driven Process." *J. of Membrane Sci.*, vol. 89, pp. 235-243, 1994.

Savitsky, A. C. and S. Siggia, "Improved Diffusion Dilution Cell for Introducing Known Small Quantities of Liquids into Gases." *Analy. Chem.* vol. 44, pp. 1712-1713, 1972.

Shah, V. M., B. J. Hardy, and S. A. Stern. 1995. "Solubility of Carbon Dioxide, Methane, and Propane in Silicone Polymers. Effect of Polymer Backbone Chains." *J. of Polymer Sci.*, vol. 31, pp. 515-517, 1995.

Shoemaker, A., T. A. Bellar, J. W. Eichelberger, and W. L. Budde,. "Determination of Polar Volatile Organic Compounds in Water by Membrane Permeate and Trap GC-MS." *J of Chromatogr. Sci.*, vol. 31, pp. 279-284, 1993.

Siegel, R. A., "A Laplace Transform Technique for Calculating Diffusion Time Lags." *J. of Membrane Sci.*, vol. 26, pp. 251-262, 1986.

Simril, V. L. and A. Hershberger, "Permeability of Polymeric Films to Organic Vapors." *Modern Plastics*, pp. 97-158, June, 1950.

Skoog, D. A., and J. J. Leary, *Principles of Instrumental Analysis*. Saunders College Publishing, New York, NY, 1992.

Slivon, Lrence E., Mark R. Bauer, Ames S. Ho, and William L. Budde, "Hellium-Purged Hollow Fiber Membrane Mass Spectrometer Interface for Continuous Measurement of Organic Compounds in Water." *Anal. Chem.*, vol. 63(13), pp. 1335-1340, 1991.

Spillman, Robert W. and Martin B. Sherwin, "Gas Separation Membranes: The First Decade." *Chemtech.*, pp. 378-384, June 1990.

Stannett, V. and M. Szwarc, "The Permeability of Polymer Film to Gases - a Simple Relationship." *J. of Polymer Sci.*, vol.16(81), pp. 89-91, 1955.

Stephens, E., "Valveless Sampling of Ambient Air for Analysis by Capillary Gas Chromatography." *J. Air Pollut.* Control Assoc. vol. 39, pp. 1202-1295, 1989.

Stern, S. A., *Gas Permeation Process in Kndustrial Processing with Membranes*. Wiley-Interscience, New York, NY, 1972.

Stern, S. A., V. M. Shah and B. J. Hardy,. "Structure/Permeability Relationships in Silicone Polymers." *J. Polym. Sci.*, Part B: Polym. Phys., vol. 25, pp. 1263-1298, 1987.

Stern, S. Alexander, "Polymers for Gas Separations: the Next Decade." *J. of Membrane Sci.*, vol. 94, pp. 1-65, 1994.

Suwandi, M. S. and S. A. Stern,. "Transport of Heavy Organic Vapors Through Silicone Rubber." *J. of Polymer Sci.*, vol. 11, pp. 663-681, 1973.

Toshima, N., *Polymers for Gas Separation*. VCH, Deerfield Beach, FL, (ed.), 1992.

Tuwiner, S. B., *Diffusion and Membrane Technology*. Reinhold Publishing Corp., New York, NY, 1962.

US. EPA, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA-600/4-84-041, Environmental Protection Agency, Washington, DC, 1987

Wang, Dongliang, K. Li, and W. K. Teo, "Effect of Temperature and Pressure on Gas Permselection Properties in Asymmetric Membranes." *J. of Membrane Sci.*, vol. 105, pp. 89-101, 1995.

Wijmans, J. G. and R. W. Baker, "The Solution-diffusion Model: a Review." *J. of Membrane Sci.*, vol. 107, pp. 1-21, 1995.

Wijmans, J. G., A. L. Athayde, R. Daniels, J. H. Ly, H. D. Kamaruddin, and I. Pinnau, "The Role of Boundary Layers in the Removal of Volatile Organic Compounds from Water by Pervaporation." *J. of Membrane Sci.*, vol. 109, pp. 135-146, 1996.

Wilks, P. A., "IR Analyzers for Ambient Air and Process Stream Monitoring." *American Laboratory*, pp. 26C-26E, 1991.

Xu, Y. H. and Somenath Mitra, "Continuous Monitoring of Volatile Organic Compounds in Water Using On-line Membrane Extraction and Microtrap Gas Chromatography System. " *J. Chromatogr.* A. vol. 688, pp. 171-180, 1994.

Yang, Min J. and Janusz Pawliszyn, "Multiplex Gas Chromatography with a hollow Fiber Membrane Interface for Determination of Trace Volatile Organic Compounds in Aqueous Samples." *Anal. Chem.*, vol. 65(13), pp. 1758-1763, 1993.

Yang, Min J. and Janusz Pawliszyn, "Extraction of Semivolatile Organic Compounds from Aqueous Samples Using High-Density Carbon Dioxide and Hollow Fiber Membrane Module." *Anal. Chem.*, vol. 65(18), pp. 2538-2541, 1993.

Yang, Min J., Yu Z. Luo, and Janusz Pawliszyn, "A Two-step Sample Prep for GC." *Chemtech.*, pp. 31-37, 1994.

Yang, Min J., Susan Harms, Yu Z. Luo, and Janusz Pawliszyn, "Membrane Extraction with a Sorbent Interface for Capillary Gas Chromatography." *Anal. Chem.*, vol. 66(8), pp. 1339-1346, 1994.

Yu, Tai-Chian, "The Effect of Chlorine, Sulfur, and Phosphorus on Deactivation of Palladium Catalysts.' Ph.D. dissertation, Dept. of Chemical Engineering, Chemistry, and Environmental Science, New Jersey Institute of Technology, Newark, NJ, 1995.

Zhang, Xin, "Continuous Monitoring of Volatile Organic Compounds in Air Emission Using Membrane Extraction Microtrap GC System." M.S. thesis, Dept. of Chemical Engineering, Chemistry, and Environmental Science, New Jersey Institute of Technology, Newark, NJ, 1994.