On-site Sample Preparation and Introduction to Ion Mobility Spectrometry

by

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A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Science

in

Chemistry

Waterloo, Ontario, Canada, 2009

DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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ABSTRACT

Solid phase microextraction (SPME), needle trap device (NTD), and membrane extraction with a sorbent interface (MESI) are solvent-free sample preparation techniques that were developed to perform the rapid routine analysis of organic compounds (VOCs) in various environmental matrices by integrating sampling, extraction, preconcentration and sample introduction procedures into one step. A portable ion mobility spectrometry (IMS) analyzer has some advantages, such as small size, light weight, operability under ambient pressure, air as carrier gas, and sensitivity, all of which make IMS suitable for on-site monitoring for low concentration of analytes.

The aforementioned sampling and preconcentration techniques were coupled with a portable IMS analyzer, as well as a thermal desorption unit that can accommodate SPME, NTD and MESI, which was modified and combined with IMS for on-site monitoring of volatile organic compounds (VOCs) from human breath and plant emissions. Experimental results demonstrated that low detection limits were achievable for gaseous analytes, (25 ng/L for acetone (SPME-IMS), 43 ng/mL (NTD-IMS) and 2.3 ng/mL (MESI-IMS) for α-pinene). These three analytical systems were applied for on-site rapid determination of acetone in human breath and α-pinene from plant emissions respectively. The salient features of these systems that make them suitable for on-site monitoring of volatile organic compounds in different sources are: small size, simple operation, fast and/or on-line sampling, rapid analysis.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor, Dr. Pawliszyn for offering me the opportunity to do research in our group and for giving me such an interesting and stimulating project.

I really appreciate my committee members, Dr. Nacson and Dr. Sloan, for their precious time spent on my project, and patience while serving as members of my committee.

In addition, I appreciate the support and suggestions from my colleagues in our group.

DEDICATION

I dedicate this thesis to my parents.

Dreams are hard to follow. Chasing dream is always a challenge. To those who help and encourage me throughout the years, thank you very much!

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

BVOCs	biogenic volatile organic compounds
CI	chemical ionization
CWA	chemical warfare agent
DVB	divinylbenzene
ECD	electron capture detector
EPA	environmental protection agency
FID	flame ionization detector
FPD	flame photometric detector
GC	gas chromatography
HPLC	high performance liquid chromatography
IMS	ion mobility spectrometry
INCAT	inside needle capillary adsorption trap
LLE	liquid-liquid extraction
LOD	limit of detection
MESI	membrane extraction with a sorbent interface
MIMS	membrane introduction mass spectrornetry
MS	mass spectrometry
NTDs	needle trap devices
PDMS	polydimethylsiloxane
PID	photoionization detector
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
R.S.D.	relative standard deviation

SOA	secondary organic aerosol
SPE	solid-phase extraction
SPME	solid phase microextraction
TAGA	trace atmospheric gas analyzer
TCD	thermal conductivity detector
TWA	time weight average
VOCs	volatile organic compounds
WHO	world health ogranization

Chapter 1. Introduction

Volatile organic compounds (VOCs) are those organic liquids or solids whose room temperature (20°C) vapour pressures are greater than about 0.52 mmHg and initial boiling points are less than or equal to 260°C.[1] The estimated world-wide average emissions of VOCs are around 1347 million tons (Mt)/year from biogenic sources and 462 Mt/year from anthropogenic sources.[2] Even though the ambient concentrations of VOCs at ug/m^3 level, exposure to VOCs still can cause toxic health effects, such as watery eyes, itching, nausea, fatigue, vomiting, and rashes. Some VOCs have carcinogenic and mutagenic effects on living organisms and human health according to the World Health Organization (WHO) and the US Environmental Protection Agency (EPA). In addition, the VOCs in urban air significantly contribute to smog photochemical reactions, which cause ozone formation, and leading to disrupting vital functions of plants (e.g., photosynthesis, growth and reproduction mechanisms.)[3] Moreover, some VOCs detected from human breath have been found to have a direct connection with specific diseases. To monitor the trace levels of VOCs from different sources, precise and accurate analytical techniques are necessary. Nowadays, the traditional analytical methods for the measurement of VOCs in the environment, plant emission or other sources in ground, air, or wastewater are usually analyzed off-site in central laboratories by conventional chromatographic methods after sampling with canisters or sorbent cartridges. The most widely applied chromatographic methods include the combination of gas chromatography with flame ionization detection (GC-FID), photoionization detection (PID) or mass spectrometry (MS). These methods are particularly useful for low level concentrations[4]; however, the response obtained from

these methods is generally time-averaged and does not provide the information required for spatial and temporal variations of concentration during sampling.[5] In addition, they offer neither real-time nor near real-time measurements and are usually time consuming. They could not provide information for making decision immediately. As such, these off-site techniques are not useful in public transport systems for monitoring the explosives, especially in the air port or subway, because the passengers should pass the security check in a short time. In such cases, on-site monitoring must be the ideal method and can provide numbers of advantages:

a. the analytical results are available immediately for making decisions in the field;
b. the portable instrumentation is mobile enough to be rapidly transported from one sampling site to another enabling a rapid response during an environmental emergency;
c. the time between sampling and analysis is effectively zero, eliminating any possible errors due to sample delivery.

An ideal measurement method should include an extraction system and instrument that are amenable to on-site monitoring. A rapid, portable, sensitive and reliable analysis method is highly desirable for environmental monitoring. The development of miniature analytical instruments for on-site monitoring of the environment has been an active area of research during the last two decades.[6,7] Some analytical approaches have therefore been developed to perform on-site monitoring of VOCs, allowing rapid and reliable evaluations of these compounds.

1.1 Instruments for on-site monitoring of VOCs

Gas chromatography is one of the most wildly applied techniques for on-site monitoring at present. Since the 1950s it has been widely used in the continuous monitoring of food, environmental, and biological samples.[8] There are many appropriate detectors which could be combined with GC for on-site monitoring, including FID, electron capture detector (ECD), PID, flame photometric detector (FPD), thermal conductivity detector (TCD), and MS. Presently, the portable gas chromatographic analytical instruments, equipped mostly with megabore capillary, isothermal temperature technology, and data acquisition system, perform with moderate selectivity and have the capability of separating 20-40 compounds in 1 to 3 minutes.[9] Despite the advantages, these commercial field-portable GC systems still face some challenges, such as their significant price tag, relatively heavy weight and large size, and relatively longer analysis time, as well as many limited to isothermal column temperature control.

Besides the GC instruments, there are also some portable mass spectrometers that have been developed since 1960 for air monitoring. One of them is TAGA (trace atmospheric gas analyzer) which is manufactured by Sciex. The latest model is a QqQ LPCI-MS^2 equipped with turbo-molecular vacuum pumps. The operation of the TAGA is based on MS^2 principles to identify and to quantify the VOCs. This method for real-time measurement of VOCs in air is simple, rugged, reliable and sensitive. But it has some drawbacks, such as with the presence of diluted $H^+(H_2O)_n$ reagent ions as a result of pressure drop and through mixing with the primary ions and high cost.[5]

Thus, a handheld or portable ion mobility spectrometry (IMS), which can detect and identify volatile and semi-volatile organic compounds with significant advantages,

such as small size and fast response, is one of the options for on-site monitoring.[6]

1.2 Ion mobility spectrometry

1.2.1 Theory of IMS

IMS, developed several decades ago, provides the possibility to work as a detector for on-site environmental monitoring. The working principle of IMS is based on the determination of mobilities in electric fields of gas phase ions derived from constituents in a sample.[10] A schematic diagram of a typical IMS, as shown in Figure 1.1, consists mainly of a reaction area and a drift region.

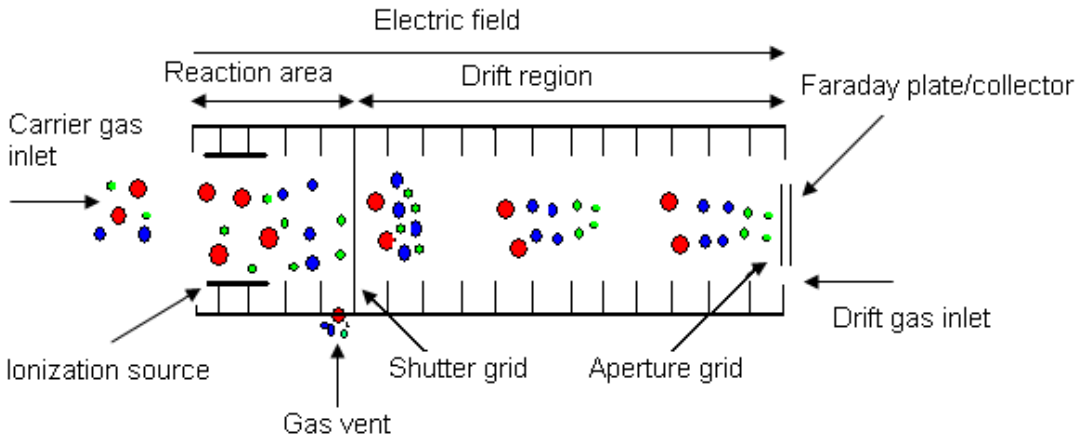


Figure 1.1 Schematic diagram of IMS.

In the reaction area, a weak radioactive ionizing source, which is generally a Nickel 63 (^{63}Ni) Beta emitter, creates reactant ions. The production of ions from ^{63}Ni starts from the emission of high energy electrons. Then the electrons collide with molecules of the supporting atmosphere, e.g. nitrogen to produce ions of N_2^+ as shown in Eq. (1.1), further reactions shown as Eq. (1.2) to Eq. (1.6) can produce positive ions, which are reactant ions for the chemical ionization of sample.[11]

$$N_2+\beta^- \rightarrow N_2^+ + \beta^- + e^- \quad (1.1)$$

$$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2 \quad (1.2)$$

$$N4^+ + H_2O \rightarrow 2N_2 + H_2O^+ \quad (1.3)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \quad (1.4)$$

$$H_3O^+ + H_2O + N_2 \rightarrow H^+(H_2O)_2 + N_2 \quad (1.5)$$

$$H^+(H_2O)_2 + H_2O + N_2 \rightarrow H^+(H_2O)_3 + N_2 \quad (1.6)$$

The IMS plasmagram is produced from the measurement of ion current by the detector. When no analytes are introduced to the IMS, only a peak corresponding to the reactant ions (hydrated protons) is observed from the plasmagram. However, when an analyte, M, is present in the reaction area it may be ionized via proton transfer:

$$M+H^+(H_2O)_{n+1} \rightarrow H^+(H_2O)_nM+H_2O \quad (1.7)$$

Dimerization may occur if the analytes are present in high concentration:

$$H^+(H_2O)_nM + M \rightarrow H^+(H_2O)_{n-1}M_2+H_2O \quad (1.8)$$

After product ions form in the reaction area, they are delivered by a shutter grid and then enter into the drift region where the ions can be accelerated by the electric field. The various ions fly towards the other side of the electric field at different but characteristic speeds and arrive at the Faraday plate (collector) with unique drift times. Small ions with compact structures have a shorter drift time while the large ions with open structures have a longer drift time. Consequently, since different ions travel in the drift region with different mobilities or drift times, they can be illustrated as distinct peaks in the ion mobility spectrum.[13] The mobility of a species, *K*, is dependent on the relationship:[6]

$$K = \frac{V_d}{E} \quad (1.9)$$

where V_d is the drift velocity, and E is the electric field gradient. K is expressed in $cm^2 V^{-1} s^{-1}$.

The mobility of ions is usually normalized to temperature and pressure and reported as reduced mobility (K_0), which can be expressed by the equation[6]

$$K_0 = K(273/T)(P/760) \quad (1.10)$$

where T is the temperature in K, and P is the pressure in torr. Reduced mobility is usually experimentally determined with an internal calibrant (reactant ion) with known mobility:[7]

$$K_0^{Unknown} = (K_0^{Calibrant} t^{Calibrant}) / t^{Unknown} \quad (1.11)$$

where t is the drift time. As mentioned above, ions with different mass and size will have different drift times and relative mobilities which can characterize analyte of interest. As well as the concentration of analyte of interest can be determined from the peak area or peak intensity.

1.2.2 Applications of IMS

IMS has many intrinsic advantages. First, fast response is the distinguishing advantage of IMS. The analysis time can be down to 10 seconds. Second, IMS has high sensitivity and analytical flexibility. The practical detection limits range from 0.1 to 100 ppb according to different target analytes.[10] Third, low power supply, small size, light weight, operability under ambient pressure and ability to use air as a drift gas make it suitable for on-site monitoring. IMS has been applied widely in analysis of chemical warfare agents (CWAs), explosives, narcotic substance and environmental monitoring. To date, most of the IMS analyzers are used for security purposes. For example, in military

areas there are more than 50,000 handheld IMS analyzers that have been used for chemical-weapons monitoring, as well as about 10,000 bench-top analyzers are employed as explosives detectors in airports worldwide, which illustrates the high reliability for on-site application of IMS.[6] Recently, increasing numbers of IMS analyzers have been applied in civilian and non-security applications, including petrochemical and environmental analysis, medical diagnostics and air quality analyses. In petrochemical, IMS is implemented to analyze for trace ammonia in ethylene and light hydrocarbon streams to ensure that the ammonia concentration in the ethylene feedstock is under control, since high concentrations of ammonia can cause catalyst poisoning in the polymerization process.[12] In the pharmaceutical industry, IMS is used in cleaning validations to confirm that reaction vessels are sufficiently clean to proceed with the next batch of pharmaceutical product.[12] In industry, the monitoring of HCl and HF in continuous source emission are regulated by government agencies. The highly corrosive nature of both compounds has made accurate monitoring at the ppb/ppm levels difficult by other analytical sampling techniques.[12] As a research tool, ion mobility has been involved in the analysis of biological materials, specifically, proteomics and metabolomics. All of the applications confirmed the advantages of IMS, which are instrumental simplicity, suitability of on-site monitoring, low cost, and extremely fast response. But IMS still faces some challenges in measurement of trace level constituents. Moreover, without pre-separation of the sample, it is difficult for IMS to provide clear cut data interpretations in case of interference from a complicated matrix.[6] Another weakness of IMS is that the sample introduced to IMS should be in the gas state. Either vaporization or additional sample separation is required

for the analysis of liquid or solid samples.[6] Thus, it is impractical to analyze VOCs present in water or aqueous samples directly. In order to analyze the low concentration of analytes and monitor compounds present in aqueous matrices directly by using IMS, different sampling and preconcentration techniques have been applied to enhance the instrumental performance.

1.3 Sampling and preconcentration techniques for VOCs

Air is a heterogeneous system composed of gases, liquids and solid particles and its composition can be affected by meteorological conditions, diffusion, and reactivity, thus sampling plays an important role on the air analysis.[13] Any mistake in sampling could seriously affect the accuracy and representative of the analysis result. In order to obtain accurate results reflecting the VOCs levels in the air, choosing an appropriate sampling method should be taken into account very carefully. There are many factors that should be considered due to their effects on the air sampling. Among them, two major key factors are likely determine if the analysis can be successful, one of them is the physicochemical properties of target analytes, while another is the expected concentration of target analytes in the air. Other factors include sampling volume and expected behaviour of the target analytes. Sampling volume must be compatible with the sensitivity of the analytical method. In addition, degradation and loss of target compounds must be eliminated.[14]

The most commonly used sampling and preconcentration methods for VOCs in air are sampling of whole air in different containers, solid sorbents trapping, solid-phase microextraction (SPME), continuous sampling and on-line analysis.[13]

1.3.1 Whole air sampling

Containers, such as stainless steel canisters, flexible plastic bags, and glass bulbs have been applied successfully for whole air sampling to determine trace organic compounds in the atmosphere.

1.3.1.1 Canisters

Canister sampling means the collection of the whole air in a pre-cleaned evacuated aluminum or stainless steel canister. It is the most commonly used method for air sampling and has been in use for 25 years. During the 1980s, the U.S. Environmental Protection Agency (EPA) adopted an evacuated canister method (TO-14 and TO-14A) targeting 40 nonpolar VOCs. In 1999, another canister sampling method, TO-15, was introduced targeting a total of 97 VOCs, including polar compounds.[15]

Canister sampling is generally performed in two modes which are grab sampling and time-integrated sampling. Samples can be collected in either sub-atmospheric (passive) pressure or pressurized (active) with pump. After sampling into the canister, sample preconcentration is carried out by using sorbent or cryogenic trap.[16] The advantages of this type of sampling are: (1) no breakthrough happens; (2) multiple analyses of the sample can be performed; (3) moisture does not affect sampling. The disadvantages are that some compounds are not stable in the canister, and sample loss or growth can occur over time, moreover, it is an expensive procedure, which requires complicated cleaning of equipment.

1.3.1.2 Plastic bags

Plastic bags are another type of container for whole air sampling. There are different types of plastic bag, such as Tedlar, Teflon and aluminized Tedlar, in various sizes, normally from 500 mL to 100 L. Plastic bags are purified by repeatedly filling the bag with pure nitrogen or clean air and evacuating them with small negative pressure. For sample collection, the bag is connected to Teflon tubing holding the bag into the area to be sampled. The pump draws a vacuum, resulting in a pressure difference, which causes the sample to be drawn through the Teflon tubing into the bag. The major advantages are that this collection method is simple and the plastic bag is inexpensive; however, some drawbacks are also obvious, such as memory effect from previous sample collection and permeability of some bags to certain chemicals.

1.3.1.3 Sampling bulbs

Sampling bulbs are used to sample permanent gases that cannot be trapped onto a sorbent. Sampling bulbs are made of glass and are equipped with two stopcock valves for sample introduction and a septum to take sample aliquots for analysis. For sampling, the gas sample can be drawn into the evacuated bulb by opening the stopcock. Analytical samples can be withdrawn through the top cap and injected into the GC for analysis. The advantages of sampling bulbs compared with the plastic bags include: the inside surface of the glass bulb is more stable than that of the air sampling bags, which can prevent the air sample from reacting with the inside surface; it is oven annealed to resist damage during transportation and on-site use; and it can be evacuated first, and then sampled without a pump. [17]

After whole air sampling by different types of containers, VOC preconcentration is usually necessary prior to analysis. Several sample preconcentration methods have been developed for this purpose.

1.3.2 Solid sorbent trapping

Solid sorbent trapping is one of the most widely used methods to monitor VOCs in ambient air. Sampling (active and passive methods) on sorbents allows the collection of a larger volume of gas than with canisters. Moreover, handling a sorbent tube is easier than handling a canister. The method can be applied at both ambient and reduced temperatures based on the properties of target analytes, for example, boiling points. The adsorbed VOCs can then be desorbed thermally or by using solvent extraction and analyzed by techniques such as GC and MS. Since this method uses sorbents for trapping samples, the selection of sorbent is critical for effective sampling compounds present in complicated sample matrix. Generally sorbents are classified as porous organic polymers, polydimethylsiloxane and carbon sorbents including activated carbon, carbon molecular sieves and graphitized carbon blanks. The amount of analyte that can be captured on the sorbents depends on the ambient condition (pressure, temperature, humidity and concentration of analyte etc.), quantity of sorbent, and sampling speed.[16] Some points should be taken into account for the selection of sorbents. First, breakthrough of the analytes has to be avoided. A combination of sorbents with differing organic strengths is beneficial for eliminating the breakthrough of analytes and trapping a wide range of compounds.[18] Second, since some sorbents may show degradation problems that should negatively affect adsorption process, these sorbents

should be taken into more careful consideration. The porous polymer resins (Tenax® TA and Tenax® GC) are reported to form artifacts while the carbon based adsorbent resins (Carbotrap B, Carbotrap C and Carbosieve SIII) are the most resistant sorbents to degradation.[19, 20] Third, moisture content remaining on sorbents has to be avoided because it can reduce the sampling rate of target analytes and result in a breakthrough problem. Carbopack B or Carbosieve SIII retained more water than Tenax® TA and Tenax® GC.[21] There are several techniques that can be used to eliminate water interference. One popular technique is to apply a desiccant tube with hygroscopic salts (K_2CO_3, $MgCO_3$, $Mg(ClO_4)_2$) in front of the sampling tube to dry the ambient air sample and without loss of the analytes.

NTDs are one type of solid sorbent trapping techniques, but use a needle for carrying sorbents. The configuration of NTDs is suitable for on-site sampling and easy to inject to different GC injectors. NTDs technique will be discussed in detail in Chapter 3.

1.3.3 Solid phase microextraction

In SPME, the analyte is adsorbed onto a fibre coated with sorbent material that projects from the needle of a syringe. SPME was developed to meet the need for rapid sample preparation both in laboratory and on-site.[22, 23] It is important to use the appropriate coating for a given application. The selection of coating depends on the physical and chemical prosperities of analytes and analysis technique, for example, gas chromatography or liquid chromatography. Since it integrates several sampling steps, such as sample extraction, sample preconcentration and sample introduction procedures into a fast and single solvent-free step, it is convenient for on-site sampling by coupling with portable

instruments, such as portable GC and IMS. The details of theory and applications of SPME will be discussed in Chapter 2.

1.3.4 On-line sampling

On-line sampling is gaining interest due to the growing requirement of on-site environmental monitoring. There are several types of on-line sampling methods that have been created, including on-line sorbent trap, membrane extraction and a technique combining sorbent trap and membrane extraction, namely membrane extraction with a sorbent interface (MESI).

1.3.4.1 On-line sorbent trap

Sorbent traps are not only used for off-line preconcentration, but also can be constructed to on-line sampling systems and coupled to suitable instrumentations for on-site analysis purposes, which allows near real-time measurement in ambient air and gaseous samples. The most frequent application of on-line sorbent trap sampling is cryogenic trapping. A Peltier device is used for cooling down the sorbent trap while sampling. But for high humidity samples, moisture can freeze in the cryotrap resulting in a plugged trap. As an alternative, a microtrap which is a small capillary tubing packed with a small amount of sorbent was introduced for on-line sampling.[24] Different from a cryotrap sampling, it is not necessary to cool the system for microtrap sampling and it is more convenient for on-line and on-site application.

On-line sorbent preconcentration has the advantage of reducing errors due to sample degradation during storage of sorbent tubes.[13] In addition to this, it offers real-time measurement which is helpful for fast decision-making.

1.3.4.2 Membrane extraction

Membrane techniques are applied for a number of diverse purposes that include microporous filtration, ultrafiltration, reverse osmosis, dialysis, electrodialysis and gas separation. When a membrane is used for extracting analytes in a sample, analytes permeate through the membrane from a donor to an acceptor phase. Supported liquid membrane extraction is the most versatile membrane extraction technique for analytical sample extraction.[25] Membrane extraction allows continuous, on-line extraction and stripping of trace VOCs from the environmental matrix. Membrane extraction has significant advantages over other sampling methods including great selectivity in enrichment, high automation potential and good capabilities for on-line analysis. Meanwhile, a relatively longer permeation time to reach a steady state is required due to boundary layer effects.

In recent years, the membrane introduction mass spectrometry (MIMS) technique has gained interest from scientists around the world. In MIMS, one side of a membrane is directly exposed to the vacuum of the ion source of the MS while the other side of the membrane contacts the bulk of sample. The organic compounds that permeated through the membrane directly enter into the mass spectrometer vacuum system. The technique is very rapid and offers increased sensitivity.

1.3.4.3 Membrane extraction with a sorbent interface

MESI consists a membrane module and a thermal desorption sorbent interface. The membrane module represents the sampling part of the system. The volatile organic compounds in the sample permeate through the nonporous membrane which directly contacts with the sample and are transported to the sorbent trap by a stripping gas from the distal side of the membrane. The membrane is the barrier between the sample and carrier gas. The nonpolar membrane prevents water or moisture in sample matrix from entering the MESI system. It also acts as a selective element since permeation rates of different molecules vary with membrane material.[26] The MESI combines sampling, preconcentration and sample introduction in one procedure, eliminating the traditional steps that cause sample loss and contamination.[27] The principle, applications, and construction of MESI will be discussed in detail in Chapter 4.

1.4 Objective

The purpose of this research was to couple SPME, NTDs, and MESI with a portable IMS analyzer with a thermal desorption unit. A universal thermal desortpion interface was modified to accommodate three sampling methods respectively. Upon investigation, the conditions of the SPME-IMS, NTD-IMS, and MESI-GC techniques were optimized in the laboratory. Finally, these systems were applied to on-site monitor acetone present in human breath and α-pinene emitted from plants respectively.

Chapter 2. Solid Phase Microextraction Coupled with Ion Mobility Spectrometry for the Monitoring of Acetone in Human Breath

2.1 Introduction

Human breath comprises numerous VOCs. The VOCs in respired air are representative of blood borne concentrations through gas exchange at the blood/breath interface in the lungs.[28] Therefore, human breath can be considered as the headspace of blood and can provide information about human health.[29] Breath analysis originated from the earliest history of medicine. In fact, the modern breath analysis began in 1971 when Linus Pauling used a cold trap for breath sampling. The frozen breath VOCs were then thermally desorbed and analyzed with a GC. Pauling found that human breath contains hundreds of VOCs with picomolar concentrations, demonstrating that human breath is a complex gas. He believed that human breath analysis could open a valuable window into the evaluation of metabolic disorders and disease conditions, as well as the measurement of early diagnosis.[30] Since then, breath analysis has attracted increasing interest. Since it is simple, noninvasive, easily repeated, low cost and more convenient compared with traditional blood and urine analysis, breath analysis therefore has the potential to replace them.

A typical human breath sample usually contains around 200 VOCs. Besides these, more than 3000 VOCs have been tested at lease once through different analysis methods.[31, 32] These compounds include endogenous compounds which may be produced in the human body and exogenous compounds which probably are absorbed from the environment. As

such, the former VOCs can only be used for diagnostic purposes.[32] Some of the major endogenous VOCs present in the breath of healthy individuals, including isoprene, acetone, ethanol, and methanol, result from normal and abnormal physiological processes.[33] Some VOCs detected from human breath have been found to have the direct connection with specific diseases. For example, a high concentration of acetone is found in the breath of a patients with diabetes mellitus, also changes in isoprene concentration have been related to acute lung injury. In addition, *n*-pentane is considered a marker of lipid peroxidation.[34] Some 28 VOCs have been identified in breath as chemical markers of lung cancer with alkanes and benzene derivates as the principal metabolic markers.[35] Most of the VOCs present in human breath are in low concentrations, ranging from ppt to ppm levels. It is impossible to analyze these trace level compounds without any preconcentration technique. The most used method is to apply solid sorption for preconcentration and followed by thermal desorption. Currently, the analytical methods for breath analysis include gas chromatography, laser spectrometry, as well as mass spectrometric methods including PTR-MS, SIFT-MS, and IMR. Philips et al.[36] applied a breath collection apparatus comprised of a portable microprocessor-controlled device and a sorbent tube for breath sampling, and the breath sample was brought back to the laboratory and trapped by a cryotrap with a temperature of 0°C. The trapped VOCs were then heated rapidly to 300°C and then the desorbed VOCs were blown away from the cryotrap and introduced into GC column. Sanchez and Sacks et al.[28] applied a multi-bed sorption trap to online preconcentrate breath samples. In this study, 25 VOCs were detected from a human breath sample. The interesting point of this study was using four types of sorbents, including

carbon molecular sieve - Carboxen 1000, and graphitized carbon blacks - Carbopack X, Carbopack B, and Carbopack Y. These sorbents were packed into the trap from top to bottom with decreasing of organic strength. This deign could avoid the moisture effect and trap wild range of organic compounds. In Pawliszyn's group, SPME used for fast sampling and MESI used for on-line sampling have been employed for human breath analysis. Grote et al.[37] used a modified SPME for breath sampling. By using a small piece of inert tubing that fit onto the SPME device, the SPME fibre can be directly exposed into the mouth of a subject. It eliminated the need of a sampling bag, avoiding the contamination from the sampling bag or degradation. A MESI technique for on-line detection of human breath was performed by a sampling chamber, membrane module, sorbent interface and GC-FID. Ethanol, acetone, isoprene and ethylene were successfully detected by this system while the moisture was blocked by the hydrophobic PDMS membrane.[29, 38] All these methods demonstrated the powerful capability for monitoring the VOCs in human breath; however, breath samples should be carried from subjects to the laboratory. It will cause sample loss during the transportation. In addition, the short half-lives of some compounds in human breath also affect the accurate measurement of human breath. On-site breath analysis is beneficial for eliminating these problems as samples are analyzed immediately after sampling. Conventionally, breath analysis has been made with instruments such as GC/MS and these are relatively large and expensive. As discussed previously, IMS, an instrument with some parallels to a mass spectrometer but with comparatively low cost, high sensitivity, high speed and small size, might be attractive for on-site use for screening of breath as a noninvasive method for routine clinical applications. SPME provides many

advantages over conventional analytical methods by integrating sampling, extraction, and sample concentration into a single step. Recently, SPME has been coupled with IMS through the design and construction of an interface for detection of volatile and semi-volatile organic explosives and drugs.[39]

2.2 SPME

SPME was developed two decades ago by Dr. Pawliszyn at the University of Waterloo, Canada. SPME is a technique that is ideally suited to field sampling. It is a solvent-free process that combines sampling, extraction, concentration and instrument introduction into a single step, eliminating complicated and time consuming sample-preparation procedures such as solid phase extraction, liquid-liquid extraction.[22] Since its advantages, SPME has been widely applied to the sampling and analysis of environmental, food, aroma, pharmaceutical, forensic, and metabolic samples.[23]

SPME passively extracts organic compounds and concentrates them onto a thin, fused-silica fibre coated with a stationary-phase material. SPME is an equilibrium, non-exhaustive extraction technique. It involves in two steps:[22] first, analytes are extracted from the matrix into the fibre coating until equilibrium is reached. Then, these analytes are desorbed thermally in the injection port of instruments. The extraction process of analytes from the sample matrix into the extraction phase, which is coated onto a fibre depends on the partitioning of an analyte between the sample matrices. The distribution coefficient between the fibre coating and the sample matrix controls the degree of partitioning for a particular analyte. If the sample matrix can be considered a homogenous phase, and there is

no headspace in the system, the amount of analyte extracted at equilibrium is given by the equation[22]

$$n = \frac{K_{es} V_e V_s C_0}{K_{es} V_e + V_s} \tag{2.1}$$

where n is the number of moles extracted by the coating, K_{es} is a fibre coating/ sample matrix distribution constant, V_e is the fibre coating volume, V_s is the sample volume, and C_0 is the initial concentration of a given analyte in the sample.

For field sampling, because the sample volume V_s is significantly larger than the volume of the fibre coating ($V_s >> V_e$), the Eq. (2.1) can be simplified to: [22]

$$n = K_{es} V_e C_0 \tag{2.2}$$

Eq. (2.2) illustrates the advantage of the equilibrium extraction method for on-site applications. In this equation, the amount of extracted analyte is determined directly by its concentration in the matrix while it is independent of the sample volume. That means there is not necessary to obtain a defined sample before analysis, because the fibre can be exposed directly to the ambient air, water, production stream, etc. As such, the whole analytical process can be simplified and then accelerated. In addition, the potential errors derived from analyte losses as a result of decomposition or adsorption on the sample-container walls are then avoided when the sampling step is eliminated.[40]

Acetone, one of the common VOCs in human breath, is produced mainly from the decarboxylation of acetoacetate, which is derived from lipolysis or lipid peroxidation. Uncontrolled diabetes mellitus causes the blood glucose to rise to excessively high levels. As a result, large quantities of acetone are produced by the human body as a function of a major metabolite.[29] Since acetone concentration was found to be much higher in diabetic

patient than that of healthy person, it has been regarded as an important disease marker of diabetes and ketoacidosis. Analysis of acetone in human breath has been used as supplementary tool for diagnosis of diabetes.[41] This study focused on the on-site application of SPME-IMS to characterize and quantify acetone in human breath. 4 min of extraction time and 15 sec of analysis time made this method suitable for rapid determination of acetone. This work will broaden the range of compounds that can be qualitatively and quantitatively analyzed by SPME-IMS.

2.3 Experimental

2.3.1 Materials and supplies

Acetone (HPLC grade) was purchased from Caledon (Georgetown, ON, Canada). Nitrogen (5.0 ultra high purity, 99.999%) was purchased from Praxair (Kitchener, ON, Canada). The SPME device, (75 μm carboxen-polydimethylsiloxane, CAR/PDMS), 65μm polydimethylsiloxane-divinylbenzene (PDMS/DVB) and 50/30μm divinylbenzene-carboxen-polydimethylsiloxane (DVB/CAR/PDMS) were obtained from Supelco (Oakville, ON, Canada). The fibres were conditioned according to the package instructions prior to use. Five healthy subjects volunteered for the breath study. Information on these subjects is listed in Table 2.2.

2.3.2 Instrumentation

A Sabre 2000 ion mobility spectrometer, obtained from Smiths Detection (Mississauga, ON, Canada) was equipped with ^{63}Ni ionization source and was programmed

in the positive mode using water as the calibrant/reactant ion. The IMS was operated with a drift tube temperature of 111 °C. The inlet temperature was set to 111 °C. The spectra were collected after a 0.1 s delay with a shutter grid width of 0.2 ms. The analysis duration was 15 s. Solid phase microextraction coupled with gas chromatography and mass spectrometry (SPME–GC–MS) analysis for the determination of acetone in human breath were performed using a Varian 3400 GC obtained from Varian Canada Inc. (Mississauga, ON, Canada) coupled with an ion trap detector. After extraction, the fibre was then inserted into the injector (200°C) of the GC and exposed for 1 min to desorb analytes collected on the fibre. A Rtx-5 column (30m×0.25mm ID, df=0.5μm) was purchased from Restek (Bellefonte, PA, USA). The column temperature was held at 30°C for 1 min and then increased by 0.5 °C min^{-1} to 35°C, where it was held for 1 min. Finally the column temperature was increased by 40 °C min^{-1} to 100°C and was held for 0.37 min, the total run time was 14 min. The carrier gas was helium at a constant flow rate of 1.5 mL min^{-1}. Data acquisition and operation parameters for the mass spectrometer were set as follows: scan range m/z 10 to m/z 200, EI auto ionization mode.

The thermal desorption (TD) unit was constructed as originally described by Liu et al.[7] The primary components of this unit are shown in Figure 2.1 and include a needle guide, T-connection connector for the gas inlet, modified SRI GC liner, obtained from SRI Instruments (Torrance, CA, USA), and a desorber/transfer line. The desorber/transfer line was made of a welded/drawn 304 stainless steel tubing (0.032 in. o.d×0.025 in. i.d.) obtained from McMaster-Carr Supply Company (Atlanta, GA, USA). A heater with a temperature control unit, designed and constructed at the Science Shop at the University of

Waterloo, was used to generate different temperatures. A PEEK connection union was used to electrically insulate the desorption device from the IMS detector. After extraction, the SPME fibre was introduced to the desorber/transfer line by passing through the needle guide. Then the fibre was exposed to the desorber/transfer line with a certain temperature. The desorbed analyte was purged into the IMS by the carrier gas flow. Different flow rates of carrier gas (nitrogen) were monitored by a flow meter manufactured by J&W Scientific (Flosom, CA, US). The desorption temperature was set to 160 °C. Figure 2.2 shows photograph of the instrument interface setup for SPME-IMS.

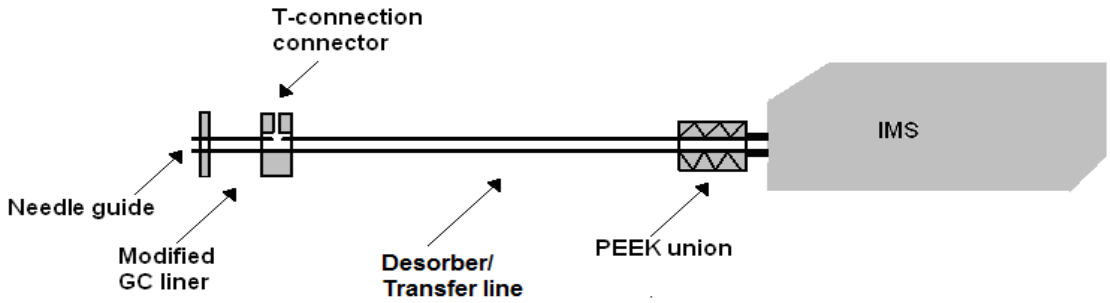


Figure 2.1 Schematic of a thermal desorption unit-IMS system: Needle guide; Modified GC liner; T-connection connector; Desorber /transfer line; PEEK union and IMS

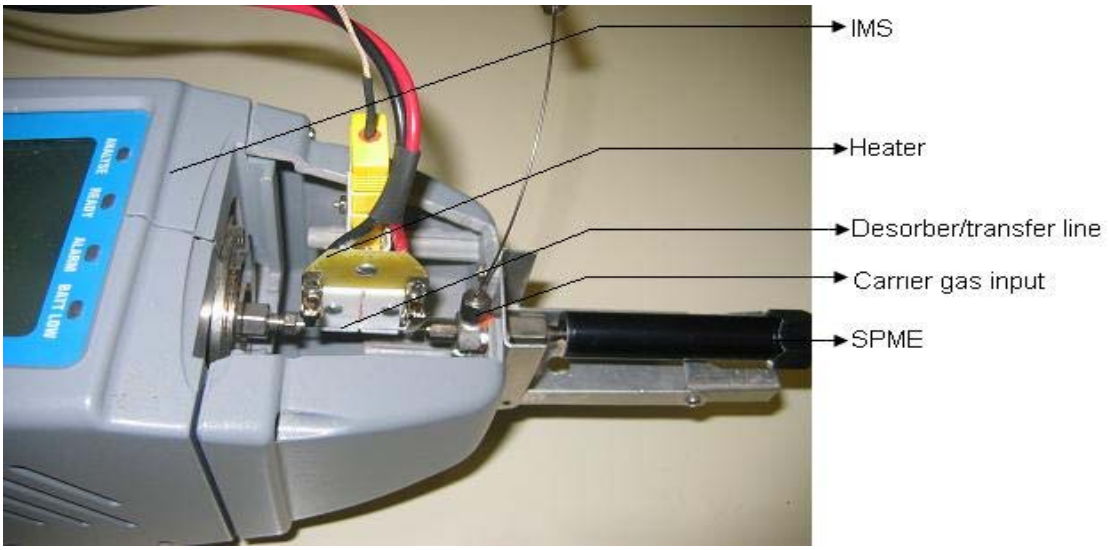


Figure 2.2 Instrument interface setup for SPME-IMS.

2.3.3 Standard gas generation

The acetone standard gas was prepared by a microwave-assisted standard gas generation system. A commercial microwave oven 1100W, model DMW1153BL from Danby (Guelph, ON, Canada) and 1 L gas-sampling bulbs from Supelco were used for standard gas preparation. The bulbs were heated in an oven then purged with nitrogen prior to use. A new piece of clean glass wool (10 mg) was set inside the sampling bulb and moistened with pure water. A thermogreen septum purchased from Supelco was used to seal the port, through which 1 – 94 μL aliquot of solution from an aqueous solution containing 25 μg/mL acetone was injected onto the glass wool. Finally the bulb was placed in the microwave oven and heated at 100% power for 75 sec.

2.3.4 Sampling by SPME

The SPME fibre was inserted into the sampling bulb for fibre selection, extraction time profile and calibration experiments. For real sampling, subjects were required to exhale breath air into a vented 125 mL glass bulb obtained from Supelco through a disposable mouthpiece. Subjects exhaled as much as possible until the glass bulb was full of breath air. For the acetone profile study, seven breath samples from one subject were obtained. For the study of acetone concentration variation before and after lunch, breath samples were collected from five subjects before lunch and after lunch (1 hour after lunch). After breath samples were collected, a SPME fibre was inserted into the glass bulb through the septum shown in Figure 2.3 and extracted for 4 min and then followed with a thermal desorption.

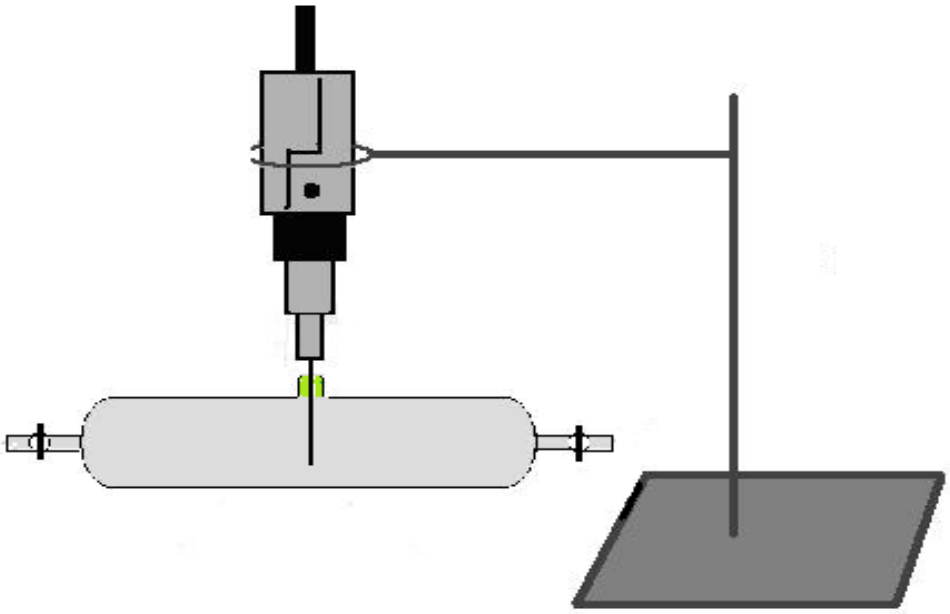


Figure 2.3 Schematic of breath sampling with SPME fibre.

2.4 Results and discussion

2.4.1 Selection of SPME fibre

The extraction ability of SPME depends on the partition coefficient value according to SPME theory. Fibres with different polymer coatings have variable K values and demonstrate different selectivities and sensitivities toward different organic compounds. As such, different fibres must be evaluated first and the optimal one can be applied for further studies. Three different SPME fibres: 50/30μm DVB/CAR/PDMS, 65 μm PDMS/DVB and 75 μm CAR/PDMS fibres were selected in this study to evaluate their ability to extract acetone. Figure 2.4 displays the results using averages of three repetitions with relative standard deviation (R.S.D.) values between 5 and 9%. The 75 μm CAR/PDMS fibre exhibits the highest sensitivity to acetone. The significant difference in extraction performance amongst the fibres probably reflects variations in the polarity of the individual

fibres. In addition, carboxen is molecular sieve that has a relatively higher surface area over DVB. In this fibre selection study, the extraction times were set to 4 minutes, which is probably not long enough for DVB/PDMS and DVB/CAR/PDMS fibres to reach equilibrium conditions for extracting acetone, since each fibrewould have its own equilibration time.

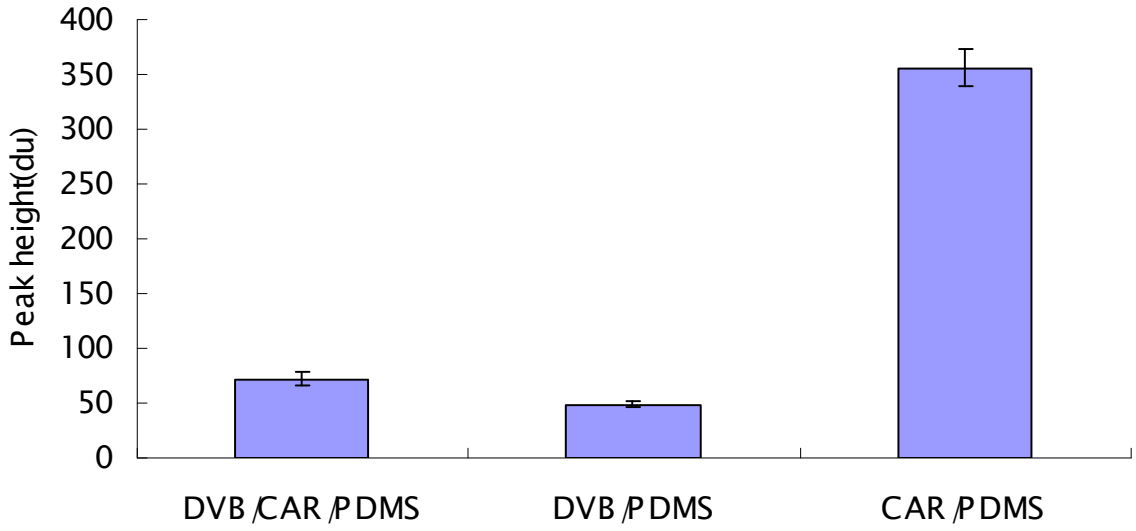


Figure 2.4 Extraction efficiency of acetone sampled by three fibres (Desorption temperature: 160 ^{o}C, flow rate of carrier gas: 10mL/min)

2.4.2 Extraction time

As SPME is an equilibrium extraction technique, the maximum amount of acetone extracted by the fibre is determined by the time to reach sorption equilibrium. The extraction time profile determined experimentally is given in Figure 2.5. The results using averages of three repetitions with R.S.D. values between 2 and 10% demonstrate that acetone approached a plateau region around 4 min (240 s). Therefore, an extraction time of 4 min allowed sufficient extraction of the analyte and was used for subsequent studies.

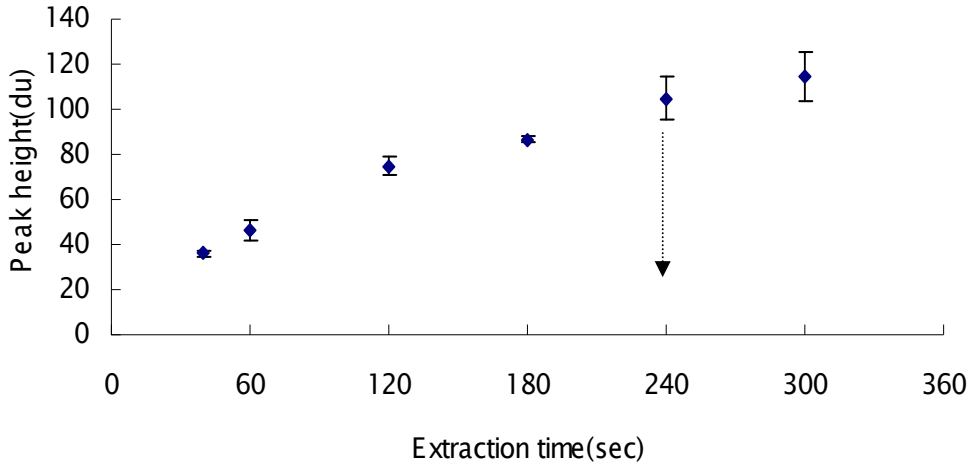


Figure 2.5 Extraction time profile obtained for acetone (150 ng/L) with a 75 μm CAR/ PDMS fibre.

2.4.3 Flow rate of carrier gas

Carrier gas flow is essential for purging analytes into the IMS for analysis. A portable cylinder with a relatively small volume of nitrogen was used for the on-site application. The results using averages of three repetitions with R.S.D. values between 3 and 13% shown in Figure 2.6 illustrates signal intensity of acetone was increased slightly with the flow rate increased from 5 to 10 mL/min. However, it decreased significantly when carrier gas flow was increased to 30mL/min. As a result, 10 mL/min of nitrogen flow was selected for this study.

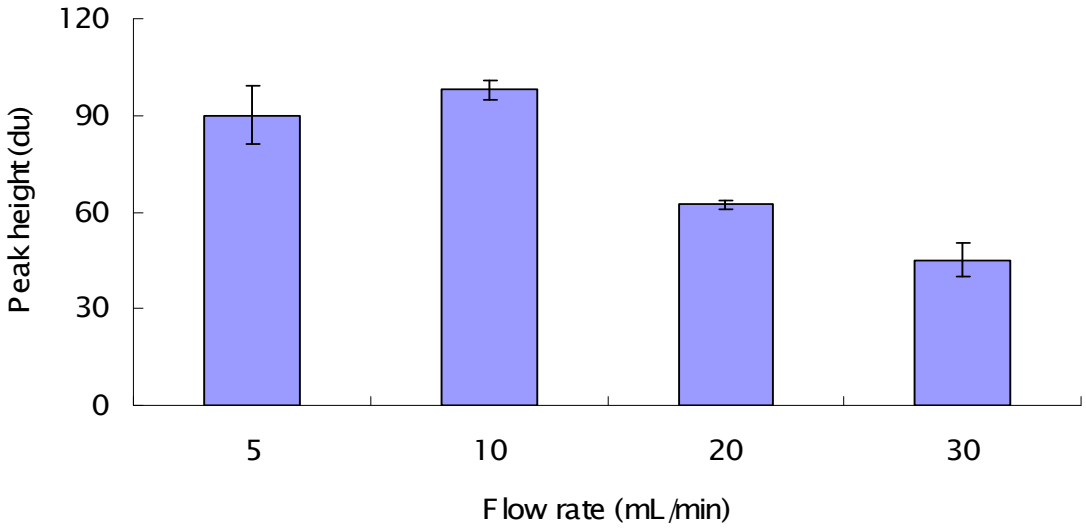


Figure 2.6 The effect of carrier gas flow rate on desorption of acetone (150 ng/L) with 75μm CAR\PDMS fibre.

2.4.4 Calibration curve

It should point out the data for calibration curve were corrected for an offset of 130 digit unit. The reasons for the offset observed could probably be due to: (1) the algorithm fixed baseline is not correct and introduced errors in the actual peak height or area; (2) electronic, acoustic and chemical noises can be strong contributors to the observed shift in the linear plot and deviation from zero point; and (3) a contaminated ion source or inlet, which a) adds on to the signal (unresolved peaks) and b) competes for the charge reservoir. The modified acetone curve is shown in Figure 2.7. Acetone was nearly linear in the concentration range between 150ng/L and 2350ng/L ($y=0.1827x$, $R^2=0.9795$) with R.S.D. of signals in the range of 4-12%. The detection limit (LOD) of acetone was 25 ng/L based on the lowest detectable peak with a signal-to-noise ration of 3:1, with a 4 min extraction time by a 75 μm CAR/PDMS fibre. The relatively low LOD of acetone is due to the higher

proton affinity of the keto-group and the formation of stable dimer of acetone.

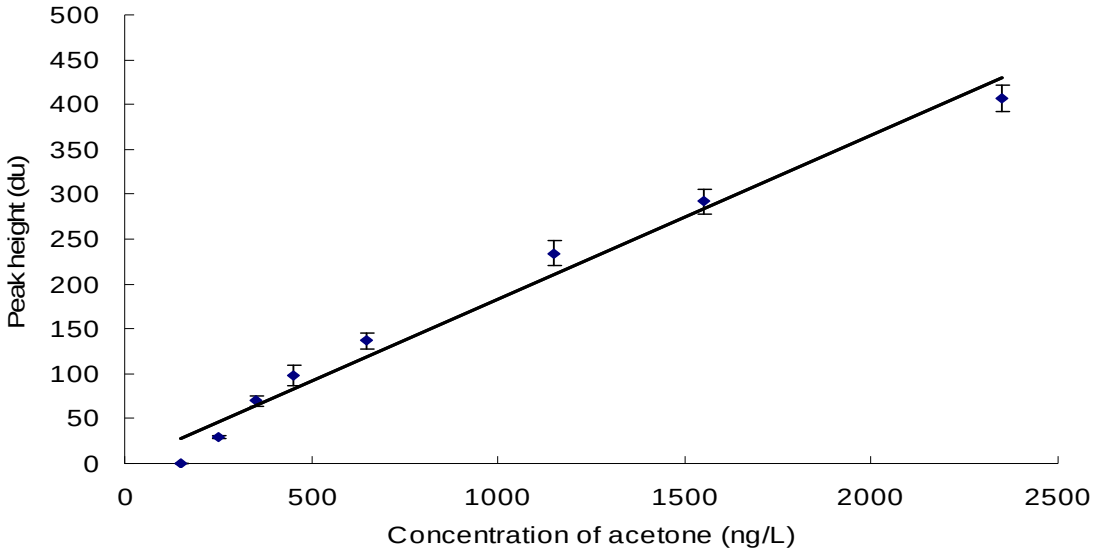


Figure 2.7 Calibration curve of acetone.

2.4.5 Reduced mobilities

A comparison was made of the drift times and reduced mobilities of acetone using conventional IMS sniff headspace vapour of pure acetone vs. SPME injection. Table 2.1 shows that the drift time and reduced mobility of acetone signal obtained from SPME injection exactly match with sniff vapour method. In addition, for the real sample analysis, the position of acetone peak also matches with SPME injection and sniff vapour method.

Table 2.1 Comparison of drift time and reduced mobility constants (K_0) between SPME, sniff vapour and breath analysis by SPME-IMS method for acetone.

	Sniff Vapour		SPME Injection		Breath analysis	
	Drift time(ms)	K_0 ($cm^2\ V^{-1}\ s^{-1}$)	Drift time(ms)	K_0 ($cm^2\ V^{-1}\ s^{-1}$)	Drift time(ms)	K_0 ($cm^2\ V^{-1}\ s^{-1}$)
Acetone	11.927	1.9291	11.923	1.9296	11.988	1.9283

2.4.6 Analysis of acetone present in human breath samples

Figure 2.8 and 2.9 show the total IMS plasma and GC-MS chromatogram of a breath sample. The peak with a drift time of 11.878 ms and a reduce mobility (K_o) of 1.9261 in Figure 2.8, which was identified by comparing the reduced mobility and mass spectrum with reference material, correspond to acetone.

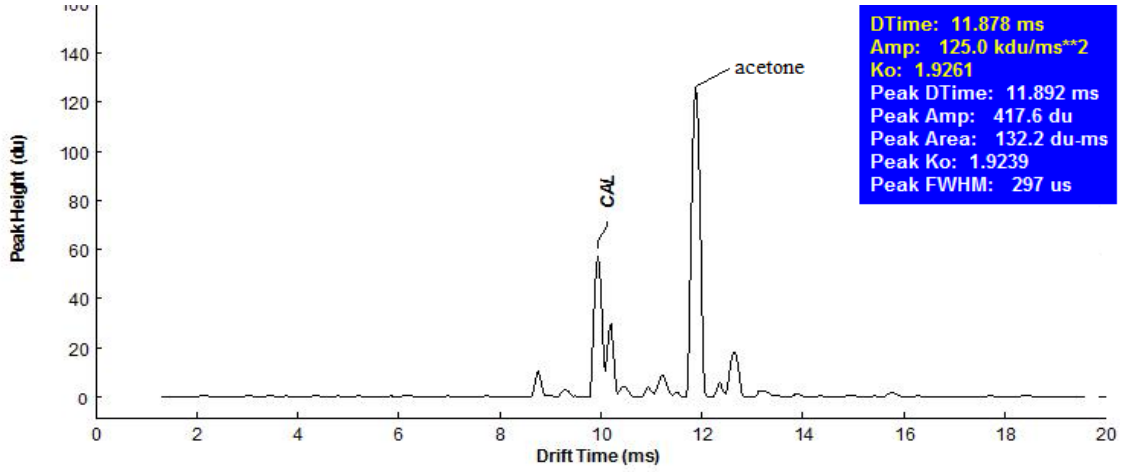


Figure 2.8 SPME-IMS spectrum obtained for acetone in human breath.

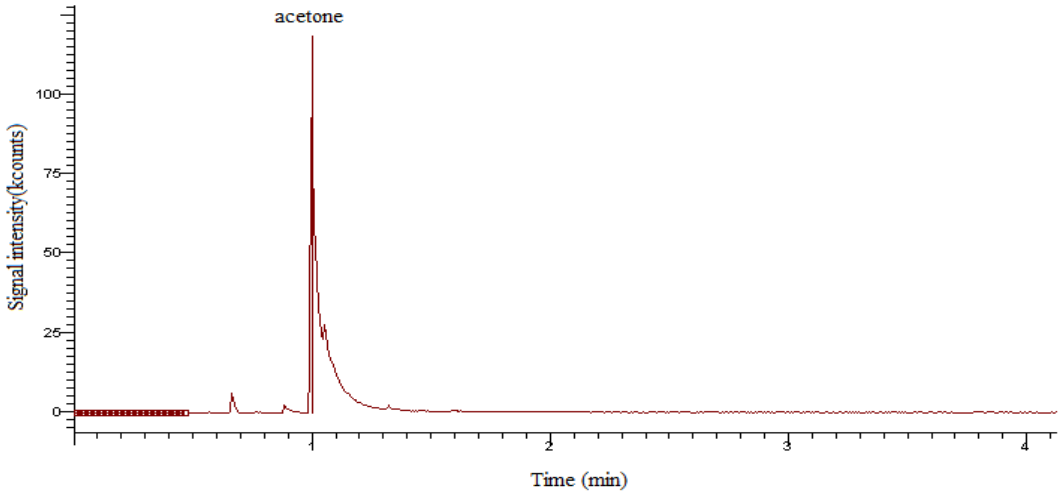


Figure 2.9 SPME-GC-MS spectrum obtained for acetone in human breath.

A male subject exhaled breath air into a 125 mL glass bulb through a disposable

mouthpiece. The subject was asked to exhale as much as possible until the glass bulb was full of breath. Seven breath samples were obtained before lunch and after dinner. The 12-hour monitoring of acetone is shown on Figure 2.10. We can see the highest levels of acetone extraction were obtained in the morning. The reason is that the subject had been fasting since dinner of the previous evening. The acetone level was still increased slightly before lunch. After lunch, the acetone level dropped down and then increased again. After dinner, the acetone level decreased again.

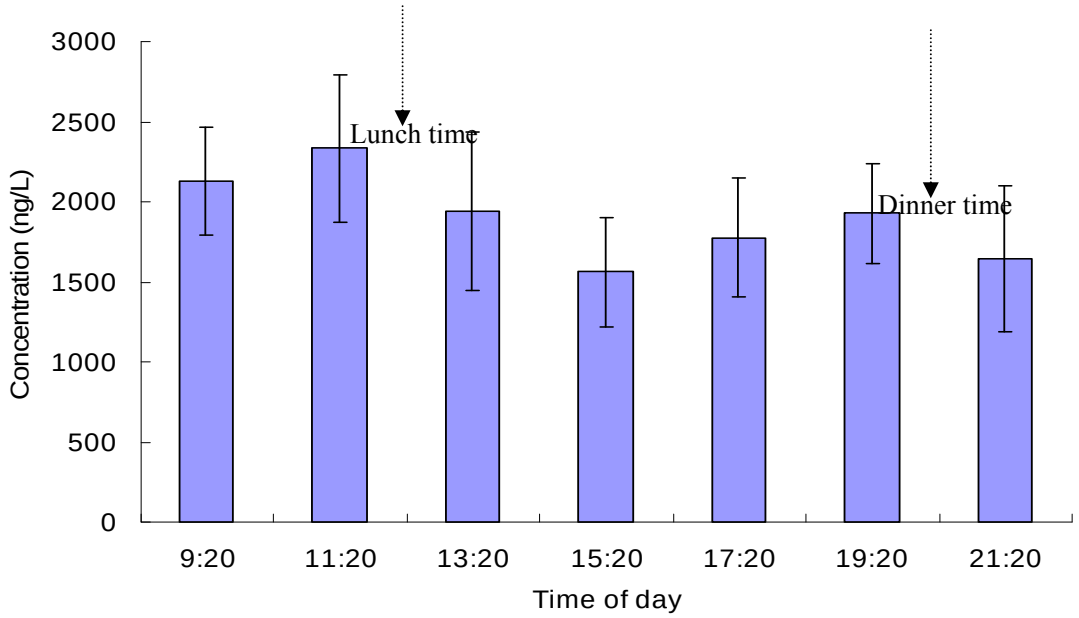


Figure 2.10 Breath acetone profile obtained from a male subject.

A similar experiment was conducted with a group of subjects that included two females and three males. Breath samples were collected from five subjects before lunch and after lunch (one hour after lunch). From Table 2.2, we observe that the five subjects possessed different acetone level in their breath, which ranged from 1573 ng/L to 2128 ng/L before lunch. After food was consumed, the acetone concentrations decreased by 5%

to 33%. The results from above two experiments confirm that the ketone bodies, like acetone, in blood increase during times of fasting or starving or during dieting.

Table 2.2 Comparison of acetone concentrations before and after lunch.

Subject	Male/Female	Age	Concentration of acetone (ng/L), n=2		Variation of acetone
			before	After	
1	M	39	1573	1353	-14.0%
2	F	33	2075	1979	- 4.6%
3	M	39	2128	1942	- 8.7%
4	F	43	1174	862	-26.6%
5	M	35	1843	1233	-33.1%

2.5 Conclusion

A 75μm CAR/PDMS fibre was selected for this study after comparing the extraction efficiencies of different fibres. A series of experiments was conducted to optimize the analysis method. A 4 min extraction time and a flow rate of 10 mL/min of carrier gas were found to have the greatest performance. The CAR/PDMS SPME coupled to IMS by using a thermal desorption unit was developed for sampling and analysis of acetone in human breath. The calibration curve obtained by sampling in the standard gas system of acetone shows good linearity within the ranges, from 150 to 2350 ng/L and a LOD of 25 ng/L was achieved. The research presented herein proves that SPME can be used for the analysis of trace level acetone present in human breath as a fast, high efficacy sample introduction technique when a hand-held ion mobility spectrometer is being used, and this method will broaden the range of compounds that are able to be qualitatively and quantitatively analyzed by SPME-IMS.

Chapter 3. Rapid Determination of α-pinene Emitted from *Pinus* sp. by Coupling Needle Trap Devices with Ion Mobility Spectrometry

3.1 Introduction

Emissions from plants contain a number of volatile organic compounds, which are known as biogenic volatile organic compounds (BVOCs). These BVOCs, other than carbon dioxide and monoxide, are commonly classified as isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$) and several oxygenated species. [42, 43] It is estimated that the global emission is around 1150 Tg per year, biogenic emissions dominate over those from anthropogenic sources by one order of magnitude.[44] BVOCs comprise a significant amount of the total VOC inventory, which have the strongly effect on the photochemistry processes. They also take part in the reactions with anthropogenic compounds in photochemical smog and tropospheric ozone.[45] Oxygenated compounds of monoterpenes oxidation would form secondary organic aerosol (SOA) through self-nucleation process[46] and partitioning to existing organic particulate matter.[47] It has been found that SOA can significantly contribute to fine particulate mass values in rural areas and affects visibility and human health as well.[48-50] Moreover, SOA may have an impact on the radiation budget and also serve as cloud condensation nuclei.[51] In addition to forming SOA, the atmospheric chemistry of biogenic hydrocarbons is also a source of hydroxyl radicals and tropospheric ozone.[52] α-pinene is one of the most abundant BVOCs among emissions from vegetation. Around 50 Tg of α-pinene is emitted per year, which is almost 45% of the estimated global annual emission of monoterpenes.[53] Thus, accurate measurement of α-pinene emissions is

critical for air quality planning in some areas, especially areas with dense forest cover. So far, several techniques have been developed for the identification, characterization, and quantification of biogenic emissions. The sampling methods have usually involved the use of macerated plants, cut plants, vacuum steam distillates or organic solvent extractives.[54] However, these sampling methods still have some challenges that cannot be ignored. One obvious drawback is that artifacts may arise during the sample preparation. For example, steam distillation may cause the formation of artifacts by heating unstable target analytes. Tissue maceration or grinding can result in the formation of enzyme-catalyzed oxidation products. Solvent extraction can introduce contaminants via the solvents. Other drawbacks of these methods are that they are time consuming, not real-time or near real-time monitoring, and often result in loss of analytes.[54] Different from the off-site analysis of BVOCs, on-site determination of BVOCs emitted from living plants are usually performed by enclosing the plant or its branch in a chamber, followed by adsorption on solid sorbents.[55] Liu et al.[54] applied an on-site application of MESI and a portable GC/FID to analysis of BVOCs emitted by a living *Eucalyptus dunnii* tree. This method provides real-time data of plant emissions. However, the relatively large size of the instrumentation and longer analysis time may limit the widespread application of this method.

An ideal sample preparation method should be solvent-free, highly selective, rugged, possess a simple design for long-term reliable performance, and it should be easy to operate for field monitoring. Like SPME techniques, NTD techniques are examples of solventless, one-step sample preparation and injection methods. The development of the NTD originated from a Tenax-filled-needle in the late 1970s. Since then, more

improvements have been achieved. In 1997, another needle trap-based sampling technique, inside needle capillary adsorption trap (INCAT) was designed by M. E. McComb et al.[56] INCAT had an adsorbing carbon coating on the interior surface of a hollow stainless steel needle and allowed sampling both the active and passive static headspace. In 2001, Dr. Pawliszyn's group developed a needle trap device that consisted of a 40 mm long 23 gauge stainless steel needle packed with a 5 mm of quartz wool.[57] It was used for airborne particulate sampling and analysis. The same research group has improved the NTD since then. The different configurations of NTDs were designed to fit the different liners of GC injector. NTDs with and without a side hole have demonstrated their capabilities for quantification and qualification of BTEX in both working and living environments and thiol compounds in vegetations. Also, a NTD packed with DVB sorbent for sampling BTEX mixture could be reused around 5000 times without losing its extraction efficiency.[58] The results show that the NTD has high reuseability. In addition, two types of simple and easily portable Time Weight Average (TWA) diffusive needle trap samplers were developed to monitor the toxic gases and vapours in both occupational and community environments.[59] The samplers can easily be carried to sites where people work and live. Since TWA sampling reflects the concentrations of target analytes in a period, the analysis results from the TWA samplings may provide the quality information of air which people are exposed to.

A needle trap is a more robust sampling device than a SPME fibre, because the sorbent materials can be protected inside a steel needle. SPME fibre's extraction capacity is normally based on equilibrium, while NTDs use a different way to extract samples.

Relying on increasing sorbent and/or sampling volumes, NTDs can easily increase the extraction capacity. Compared to conventional sorbent traps, NTDs are more convenient sampling/sample preparation tools since it can provide important advantages for on-site sampling, as cryogenic focusing technique is not required during desorption due to using micro-sized tubing that contains very low amounts of sorbent. In addition, needle-like devices are particularly convenient for automation and development of on-line procedures.

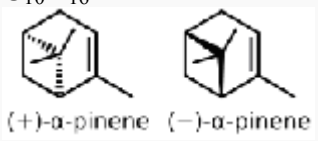
Active NTD sampling is an exhaustive sampling method. If the sampling volume is smaller than the breakthrough volume, the concentration of an analyte (C_0) can be calculated with the equation below:

$$n = C_0 V \tag{3.1}$$

where n is the mass extracted by the NTD, C_0 is the concentration, and V is the sampling volume.

The NTD technique has been used to investigate VOCs in air and vegetation. The majority of these studies have been performed in the laboratory. In this study, NTD coupled with a portable IMS analyzer was performed for the rapid determination of α-pinene emitted from a *pinus* sp. The physical and chemical properties of α-pinene are listed in Table 3.1.

Table 3.1 Properties of α-pinene.

Molecular formula and structure	Molar mass	Appearance	Density	Boiling point	Solubility in water	Proton Affinity
$C_{10}H_{16}$ 	136.23 g/mol	Clear, colourless liquid	0.858 g/mL (liquid at 20°C)	155 °C	Very low	204 kcal/ mol

3.2 Experimental

3.2.1 Materials and supplies

α-Pinene (analytical grade) was purchased from Sigma-Aldrich (Oakville, ON, Canada). Nitrogen (5.0 ultra high purity, 99.999%) was purchased from Praxair (Kitchener, ON, Canada). Carboxen 1000 (60/80 mesh) was purchased from Supelco. Hypodermic stainless steel needles (22 gauge) were purchased from DynaMedical Corporation (London, ON, Canada). A stainless steel hypotubing, 20 gauge, was purchased from Small Parts Inc. (FL, US). A thin, soft stainless steel wire (100 μm diameter) was used to make a stainless steel spring stopper for holding sorbents in the needle. A living branch on a *Pinus* sp. growing on campus was monitored on-site.

3.2.2 NTD Construction

The 22-gauge needles were selected for the construction of NTDs for this study. If the needle was too small, it was easily resisted or even was blocked by sorbents during packing. The finished needle trap is illustrated as Figure 3.1. The procedure to prepare a NTD is as follows: a steel spring stopper was placed into the needle by pressing it between

two guide wires and fixed in the required place. The steel spring stopper was used for immobilizing the sorbent firmly while packing. The location of it depended on the amount of sorbents or the bed length of sorbents; then an aspirator was used to aspirate the sorbent into the needle until it came to the required place. A guide wire was used to push the sorbent to reach the required position. Carboxen 1000 sorbent was packed into the needle to form a needle trap with a bed length of 15 mm. The strength of packing should be taken into careful consideration because loose packing caused a small breakthrough volume while compact packing resulted in high flow restriction; finally, another steel spring stopper was plugged into the needle with a guide wire. As such, the packed sorbents were firmly held in place by two steel spring stoppers at both sides of the needle, preventing sorbents from bleeding during the thermal desorption step. The NTD was then conditioned in a SPME conditioning tool at 270°C for 2 h to remove impurities.

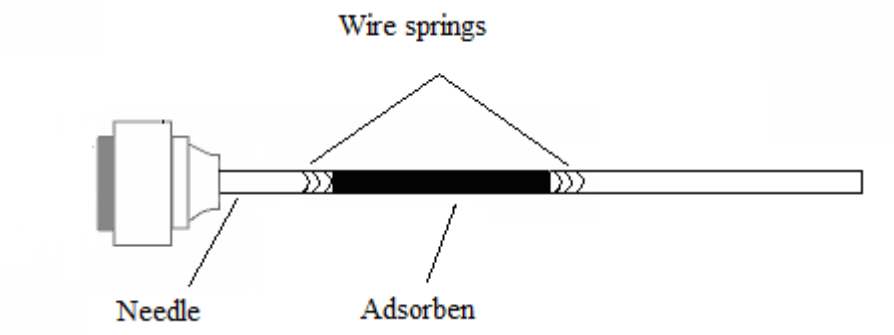


Figure 3.1 Schematic of the NTD packed with Carboxen 1000 sorbents.

3.2.3 Instrumentation

A Sabre 2000 ion mobility spectrometer, obtained from Smiths Detection (Mississauga, ON, Canada) equipped with ^{63}Ni ionization source and was programmed in the positive mode using water as the calibrant/reactant ion. The IMS was operated with a

drift tube temperature of 111 °C. The inlet temperature was set to 200 °C. The spectra were collected after a 0.1 s delay with a shutter grid width of 0.2 ms. The analysis duration was 30 s. The flow rates of carrier gas were monitored by a flow meter manufactured by J&W Scientific (Flosom, CA, US).

A thermal desorption unit used for SPME-IMS study was modified for this study. The needle guide and desorber/transfer line were replaced to accommodate the needle trap since the different outer diameters between the SPME and a needle trap. A 20 gauge stainless steel hypotubing was used for the desorber. The components of this thermal desorption unit is shown in detail in Chapter 2. After sampling, the sorbent trap was inserted into the desorber, which was heated at a certain temperature using a power supply, designed and constructed at the University of Waterloo Science Shop. Figure 3.2 shows a photograph of the instrument interface setup for NTD-IMS.

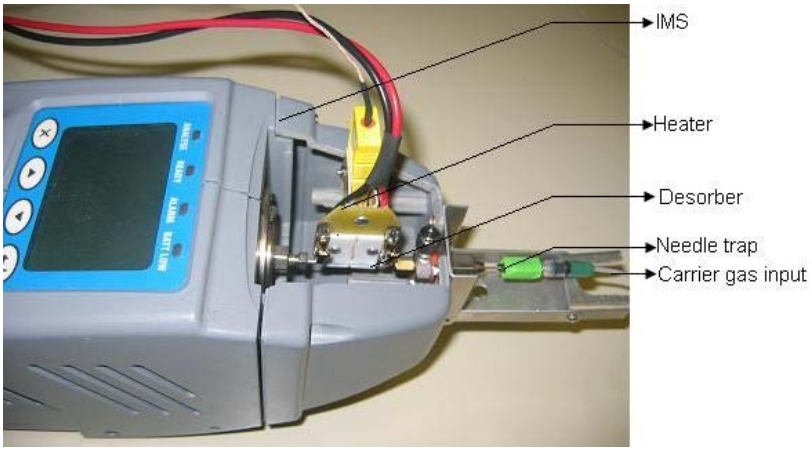


Figure 3.2 Instrument interface setup for NTD-IMS.

3.2.4 Standard gas generation

The procedure of standard α-pinene gas generation was the same as that of acetone generation described in section 2.3.3. 2.5 to 15uL aliquot of the standard methanolic

solution of α-pinene (10%) was injected onto the glass wool.

3.2.5 Sampling by NTD

A bidirectional syringe pump purchased from Kloehn (Las Vegas, NV, USA) was used to obtain accurate sampling rates and sampling volumes for experimental studies in the laboratory. During the on-site sampling, a branch from a *Pinus* sp. was enclosed in a plastic bag for 50 min before NTD sampling. A sampling volume of 10 mL air in the plastic bag was obtained by a manual sampling pump (AP-20) obtained from Komyo Ricagaku (Kanagawa, Japan).

3.3 Results and discussion

3.3.1 Effect of desorption temperature

The boiling point of α-pinene is relatively high and the affinity between the compound and packing materials are strong, so the system should exhibit carryover without a suitable desorption temperature. Figure 3.3 shows the results of desorption temperature profile obtained from averages of five repetitions with R.S.D. values between 6 and 14%. The response of α-pinene increased as the desorption temperature was raised from 180°C to 260°C. As expected, the carryover of analyte also decreased considerably at higher temperatures. At 260°C the carryover of α-pinene could not be eliminated completely with a single injection and consistently exhibited approximately 8.5% carryover while there was a 44% carryover with a desorption temperature of 180°C. Since the desorption duration was only 30 seconds, it was beneficial to add a cleaning step of two

injections to the method after each analysis to ensure no carryover of analytes.

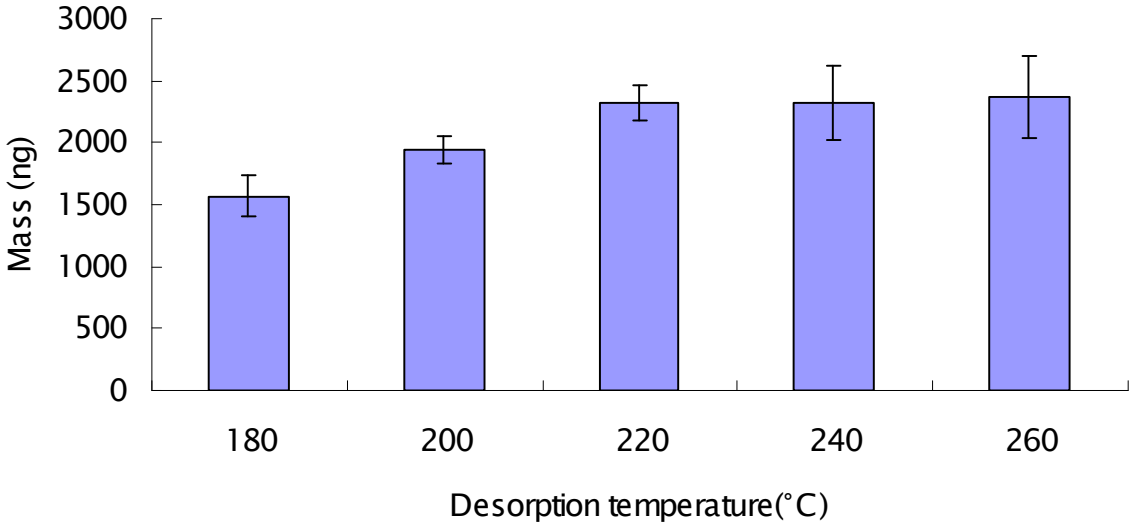


Figure 3.3 Effect of desorption temperature on desorption efficiency of α-pinene (concentration: 430 ng/mL, sampling volume: 5 mL, carrier gas flow rate: 10 mL/min)

3.3.2 Effect of flow rate of carrier gas

Carrier gas is applied to purge the extracted analytes on the sorbent material. For on-site monitoring purposes, applying a reasonable flow rate of carrier gas will lower the cost of analysis and extend the use of the carrier gas. Figure 3.4 shows the flow rates increased from 10 mL/min to 20 mL/min, the signal of α-pinene increased slightly. However, no significant difference was found between different flow rates of carrier gas. It means the flow rate did not affect the desorption efficiency of α-pinene. As a result, 10 mL/min of nitrogen flow was selected for this experiment.

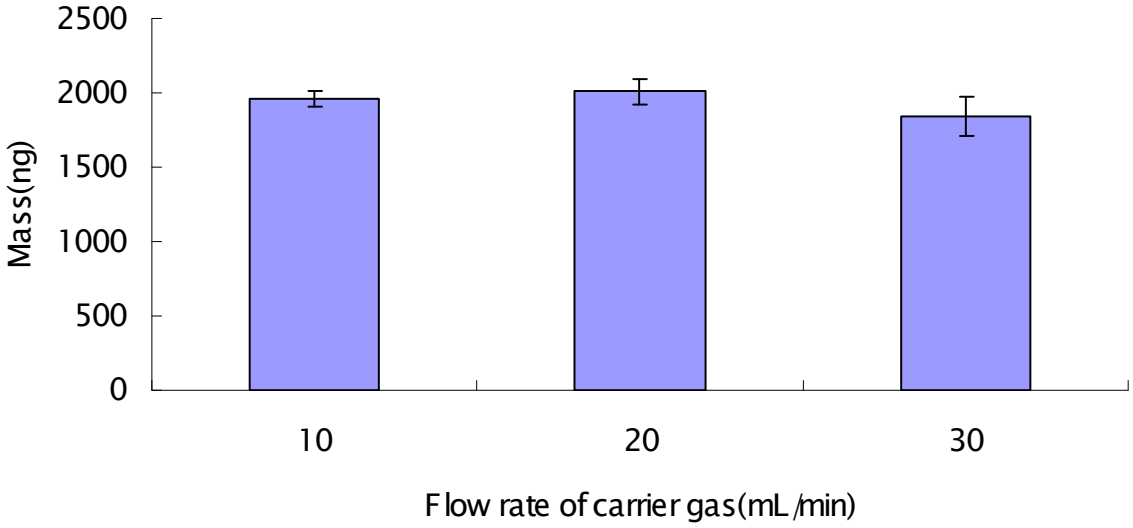


Figure 3.4 Effect of flow rate of carrier gas on desorption efficiency of α-pinene (concentration: 430 ng/mL, sampling volume: 5 mL).

3.3.3 Effect of sampling volume and breakthrough investigation

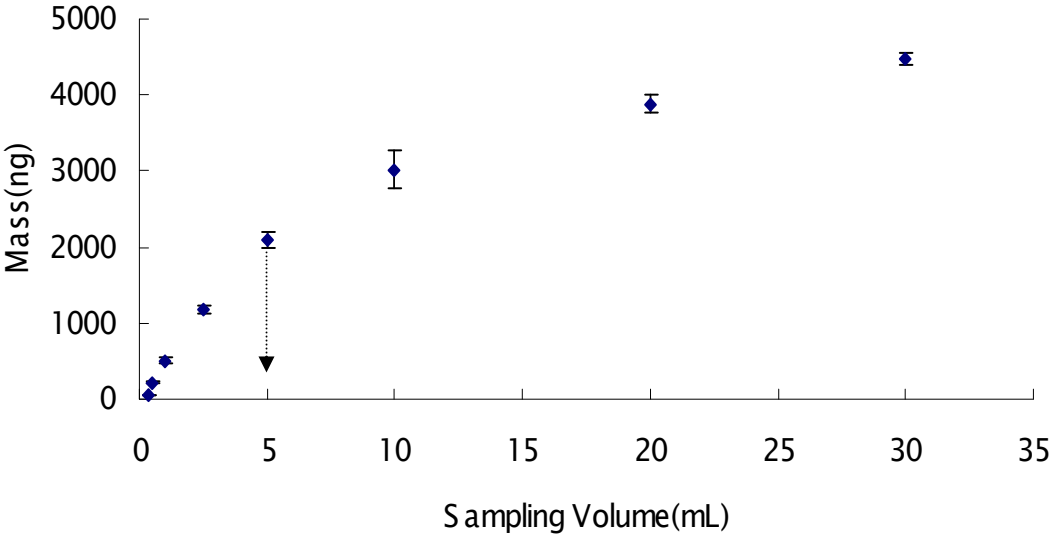


Figure 3.5 Effect of sampling volume on the extraction efficiency of α-pinene (concentration: 430 ng/mL).

Sampling volume is another important parameter for needle trap application

because it can influence detectability. Different sampling volumes were used for sampling α-pinene. Figure 3.5 shows the IMS response against sampling volumes. By increasing sampling volume, the signal was increased. The response increased significantly when the sampling volume was increased from 0.38 to 5 mL; the rate of increase was reduced after that point, indicating breakthrough had occurred. Since sampling volume is concentration dependent, the results will likely change as the concentration of analyte changes. If concentration decreased, a larger sampling volume will be possible before breakthrough.

It is very important to investigate the breakthrough volumes when NTD is used for active sampling that is in the exhaustive extraction mode. The breakthrough volume could be affected by different factors, such as the amount of the packed sorbent, the density of the packing, the volatility and the affinity of the target analytes. In this study, two methods were applied to test the breakthrough volume. First, the NTD packed with Carboxen 1000 was inserted into the sampling bulb to extract α-pinene. After collecting a certain volume of air in the bulb, there was the same volume of after-extraction air remaining in the syringe. The first sampling needle trap was disconnected from the syringe and a second clean needle trap was connected to the syringe. The after-extraction air was injected into the clean needle trap. This needle trap was then introduced into the IMS immediately to analyze for any remaining α-pinene in the air. With the sampling volume increased to 10 mL, a small α-pinene peak appeared in the IMS plasma and it meant breakthrough had occurred with a 10mL sampling volume.

The second breakthrough investigation method was conducted by connecting two NTDs packed with Carboxen 1000 in series with a universal GC column connector. The

hub of the front NTD was cut so that it could be coupled with the back NTD. For the breakthrough study, the back NTD was connected to the sampling pump, and the front NTD was inserted into the sampling bulb. The sample was drawn through the two NTDs at a sampling rate of 5mL/min. The sampling volume was increased until α-pinene extracted by the back NTD could be detected by IMS. It was observed that the breakthrough volume of α-pinene was 12.5 mL, which was close to the breakthrough volume of the first method.

3.3.4 Reproducibility

The reproducibility of the carboxen NTD device for α-pinene with a sampling rate of 2.5mL/min and a sampling volume of 5 mL is summarized in Table 3.2. Good precision was observed for the same NTD (2-11% R.S.D.) as well as for four different NTDs (7% R.S.D.) despite the fact that it was constructed by a manual packing system. The reproducibility from different NTDs results from the packing quality variation; however, operating the NTDs under breakthrough volumes and in the exhaustive sampling mode may minimize the variability.

Table 3.2 Reproducibility result for the Carboxen NTD (intra-NTD) and between three different NTDs (inter-NTDs).

	NTD1(n=3)	NTD2(n=3)	NTD3(n=3)	NTD4(n=3)	All(NTD1-4) (n=12)
R.S.D., %	11	3	2	8	7

3.3.5 Storage time for Carboxen NTD with loaded α-pinene

Storage time depends on the affinity strength between sorbent material and target analytes. Two NTDs packed with Carboxen 1000 were applied for the storage study. After sampling α-pinene, the NDTs were plugged with Teflon stopper to prevent ambient air from entering into the NDTs and then stored at room temperature (~24°C). After a certain time, the NTDs were inserted into IMS for analyzing α-pinene. The peak heights of α-pinene obtained by the two NTDs were compared individually with the responses obtained by injections done immediately after sampling by the same NTDs. The results are 96% and 95% recovery for 48 hours post-sampling. There was no significant sample loss during the two day storage.

3.3.6 Comparison of pump sampling and manual sampling

A pump is convenient for sampling with controlled sampling rate and sampling volume in the laboratory; however, it is not suitable for outdoor and on-site sampling. Also, the pump is not useful for areas without a power supply. As such, a syringe for manual sampling is a good alternative. In order to compare these two sampling tools, a 5 mL/min flow rate was applied for this study. The sampling efficiency of manual control is almost the same as that of pump control. Peak intensity of α-pinene with manual control sampling was as 97.9% as that of pump control.

3.3.7 Calibration curve

An average of three repetitions was used for each of the six concentration values to create the external calibration curve for α-pinene. As discussed in Section 2.4.4, the data

for calibration curve were corrected for an offset of 49.6 digit unit. The modified calibration curve shown in Figure 3.6 demonstrates good linearity with a concentration range from 215 to 1290 ng/mL (y=0.14x). The R.S.D. values ranged from between 2 and 9%. A correlation value of 0.9734 was obtained with a limit of detection (LOD) 43 ng/mL.

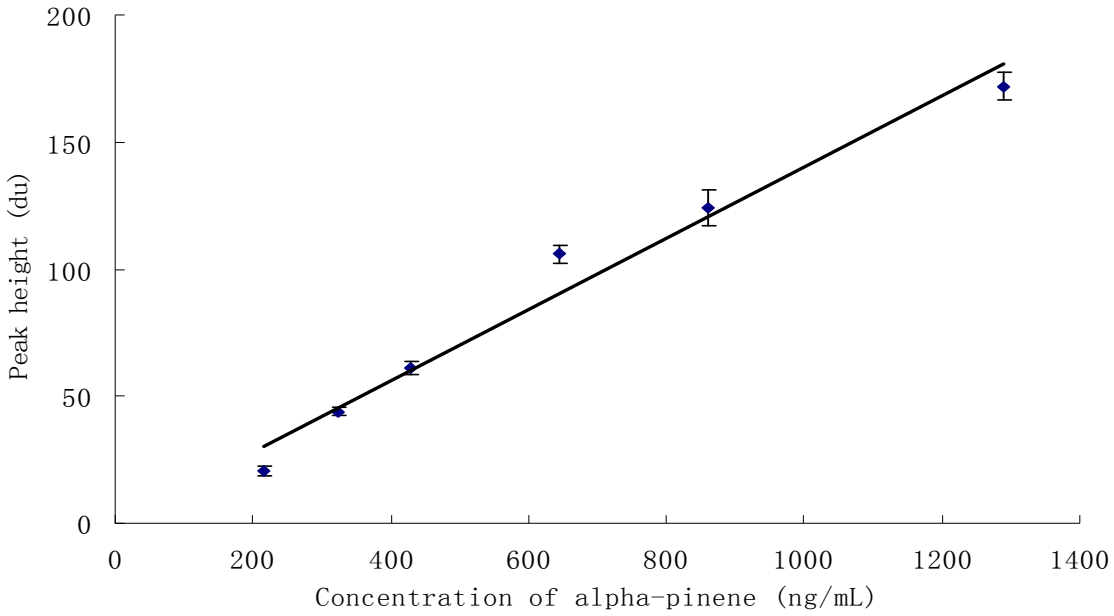


Figure 3.6 Calibration curve for α-pinene (sampling volume: 1 mL).

3.3.8 Analysis of α-pinene emitted from a *Pinus* sp. branch

Figure 3.7 shows the IMS spectrum obtained for the extraction of α-pinene emitted from a *pinus* sp. branch. A plastic bag was used to enclose a branch of a *pinus* sp. on the University of Waterloo campus. After the branch was enclosed in the plastic bag for 50 min, a Carboxen 1000 NTD was used for sampling with a syringe, and 5 mL air was drawn from the enclosed bag. The concentration of α-pinene emitted from the branch of *pinus*. sp was 747 ng/mL.

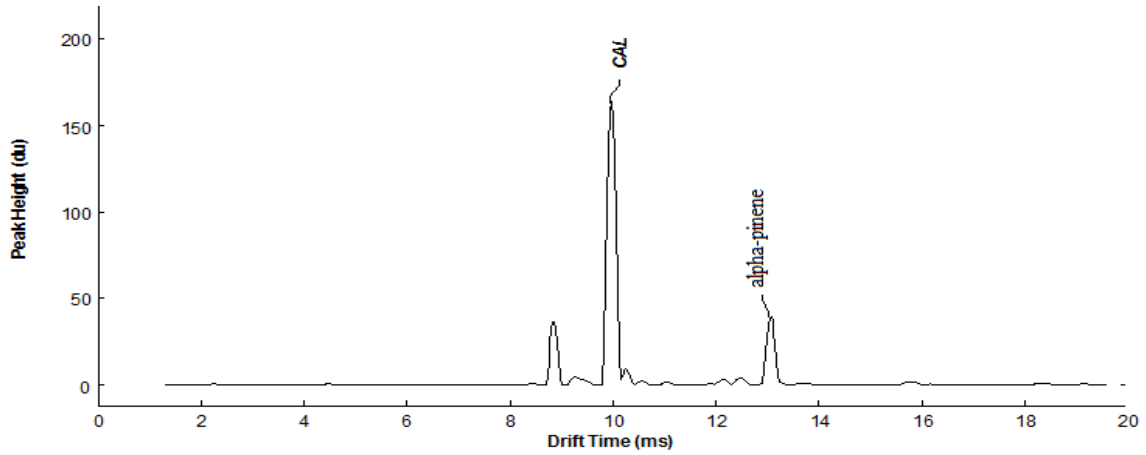


Figure 3.7 NTD-IMS spectrum obtained for extraction of α-pinene emitted from a *pinus* sp. branch

There are many factors that can affect the biogenic emission, including ambient temperature, vegetation type and density and humidity.[60, 61] Experiments were conducted to monitor α-pinene emission from the *pinus* sp. during a two-day period. A plastic bag was used to enclose a branch of *pinus* sp. 50 min before sampling and then 10 mL air in the plastic bag was sampled by a NTD. Figure 3.8 shows the results of monitoring α-pinene emissions on two separate days. We can see the concentrations of α-pinene of Day 2 were higher than that of Day 1, which may be related to the fact that the highest outdoor temperature of Day 2 was 30 ^{o}C which was much higher than that of Day 1 (23^{o}C). One interesting result was obtained from the last analysis of Day 1. The concentration of α-pinene increased 83% from the previous data point and reached the highest concentration observed on Day 1. This was despite the fact that emissions were expected to decrease at that time due to the temperature and time of day. The reason was probably the effect of rain on the emissions. Lamb et al.[62] reported that *α*-pinene emissions from wetted vegetation surfaces (rain or dew) were approximately 10 times larger than from dry branches at a

given temperature. Janson et al.[61] found similar results. He reported a higher emission rate occurred when Scots pine and Norwegian spruce were wet. Therefore, it is suggested that the variations of α-pinene emission are a result of the variations of temperature and humidity conditions during the sampling days.

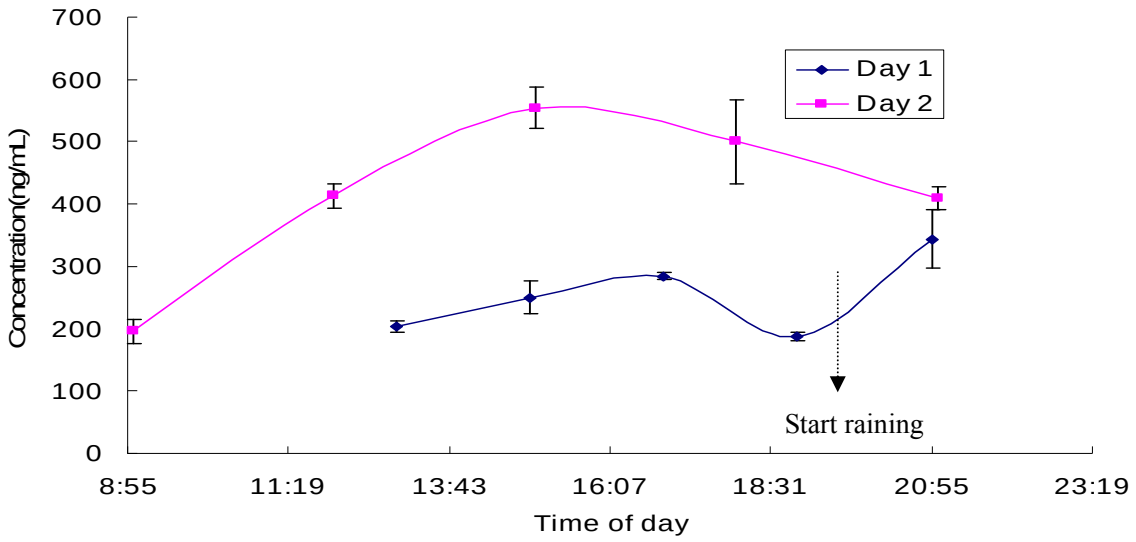


Figure 3.8 Profiles of α-pinene emitted from a *pinus* sp. branch in two days.

3.4 Conclusion

The NTD technique is a solvent-free sampling and preconcentraion method for sampling and analyzing volatile organic compounds from many different sample matrices. It has several advantages, such as inexpensive, robust, reusable, easy operation. In this project, needle trap devices were combined to IMS with the thermal desorption unit. The NTD-IMS system was conducted for on-site sampling and determination of α-pinene emitted from *pinus* sp. The results indicate that NTDs coupled with a portable IMS can provide a convenient and sensitive on-site sampling technique for sampling and analyzing volatile organic compounds.

Chapter 4. Rapid Determination of α-pinene Emitted from Peppermint by Coupling MESI with Ion Mobility Spectrometry

4.1 Introduction

Membrane extraction with a sorbent interface (MESI), a sample preparation method developed by Dr. Pawliszyn, has been involved in rapid analysis and on-line continuous monitoring of VOCs present in waste water, air and human breath since it was designed.[63] Figure 4.1 outlines the MESI-IMS system. The system consists of four main parts: (1) the membrane module; (2) the sorbent interface with a heating and cooling unit; (3) detection system and (4) data acquisition system. The membrane module represents the sampling part of the system. A nonporous membrane is sandwiched in the module. The feeding side of the membrane contacts directly with the sample. The volatile organic compounds from the sample permeate through the membrane and reach another side of it. The permeated compounds then are carried by the stripping gas (carrier gas) to the sorbent trap where they are preconcentrated. When the maximum amount of analytes are trapped by the sorbent trap, a desired high temperature is applied to the sorbent trap by a thermal desorption unit. Finally the desorbed analytes are introduced into the detection instrument for analysis. The MESI system has significant advantages over the traditional sampling and sample preconcentration techniques:[64]

a. it is solvent free
b. sampling, preconcentration, and sample introduction are integrated in one procedure, eliminating the multiple steps that cause sample loss and contamination
c. it has high sensitivity and good selectivity

d. it can be used on-site and on-line for monitoring of air and water

e. it easily combines with different instrumentations

f. it is inexpensive

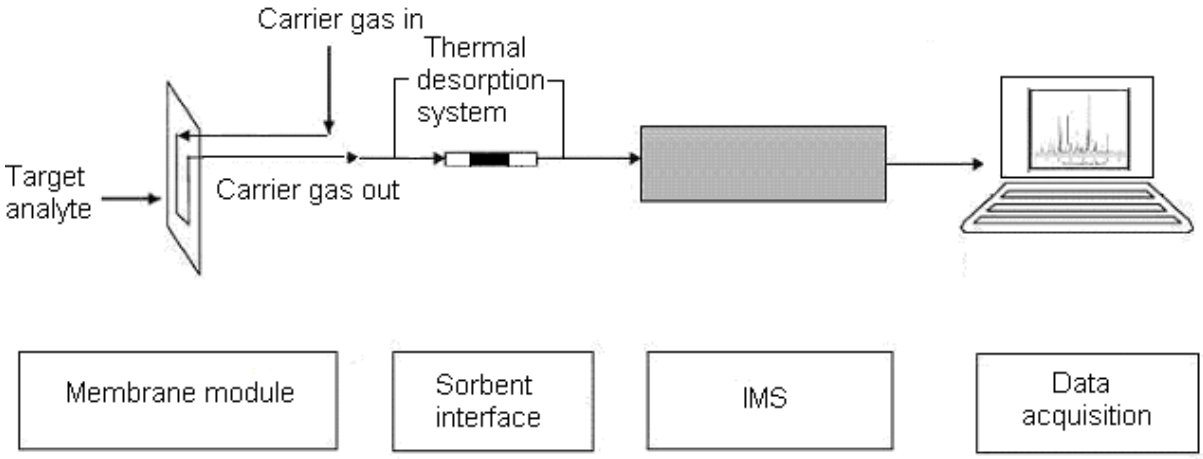


Figure 4.1 Schematic diagram of MESI-IMS system.

4.1.1 Theory of MESI

The mass transfer of volatile organic compounds through a nonporous polymer membrane is generally described in terms of a "solution-diffusion" mechanism.[65, 66] The mass transfer of the target analyte processes consist of several steps as described in Figure 4.2: (1) mass flux of analyte from air to the boundary layer outside the membrane surface, convection and diffusion processes; (2) diffusion of analyte through the boundary layer to the membrane outer surface, a diffusion process; (3) partition of analyte between air and membrane at the membrane outer surface, a partitioning process; (4) random movement of the analyte in and through the membrane, a diffusion process; (5) release and stripping of analyte by carrier gas at the inner surface of the membrane, a partitioning process; (6) diffusion of analyte though the gas boundary layer, which is close to the inner membrane

surface, a diffusion process; (7) mass transfer away from the membrane surface by the stripping phase, diffusion and convection processes.[67]

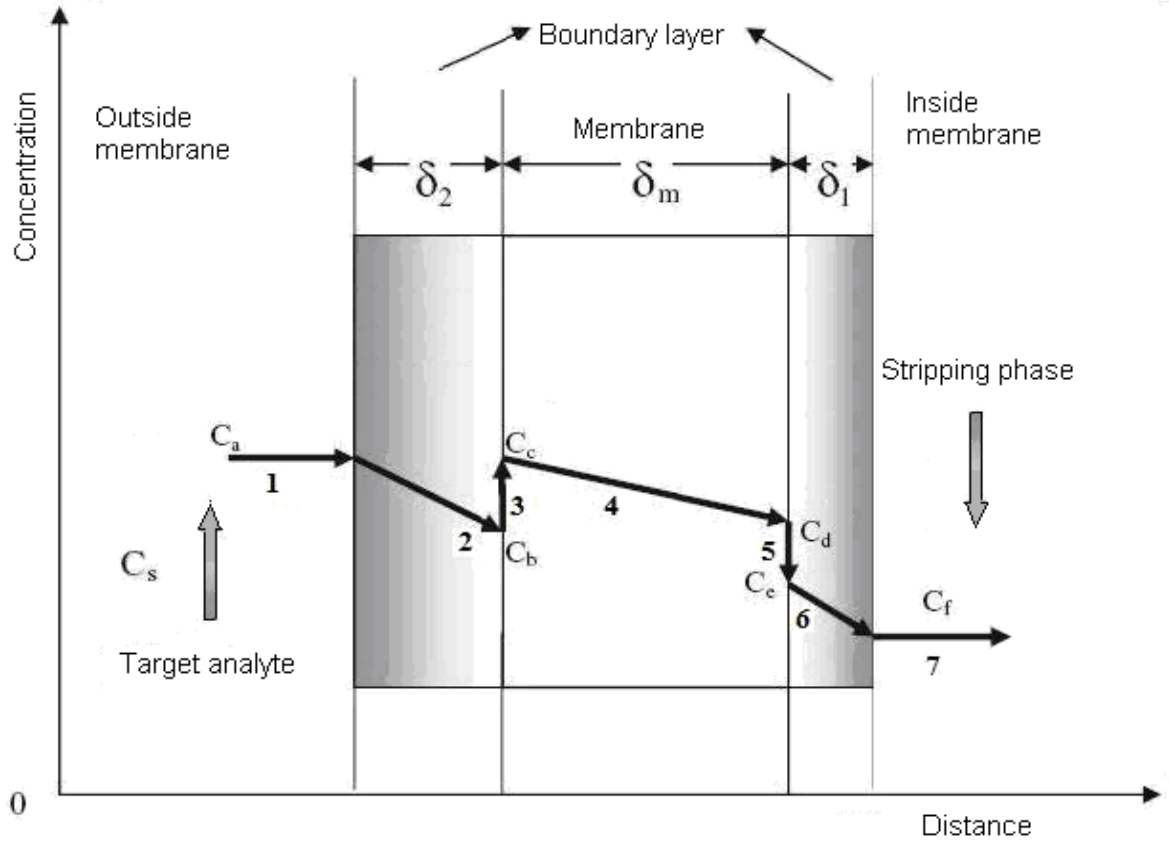


Figure 4.2 Membrane extraction processes and concentration gradient of a target analyte (1) Convection and diffusion; (2) Diffusion; (3) Partitioning; (4) Diffusion; (5) Partitioning; (6) Diffusion; (7) Diffusion and Convection

Calibration is an important aspect in the application of MESI for sample analysis, as seen in other methods based on membrane extraction. When the membrane extraction is operated under good agitation in both the sample matrix and the stripping gas at constant temperature, the diffusion through the membrane controls the mass transfer rate of the analytes. In this case, the external calibration method[68] can be used to provide good precision and a wide dynamic range. Assuming a steady state, the sample concentration of

the unknown (*Cs*) can be obtained by [67]

$$C_s = \frac{bn}{B_2 A D_e K_{es} t} = Zn \tag{4.1}$$

where b is the thickness of the membrane, n is the extracted amount of analyte in the sorbent trap in a period of extraction time (t), A is the surface area of the membrane, D_e is the diffusion coefficient of the analyte within the membrane, K_{es} is the membrane/sample matrix distribution coefficient, and B_2 is a geometric factor defined by the shape of the membrane, also where $Z=b/B_2AD_eK_{es}t$ is a calibration constant, which can be measured in advance using the standard gas containing a given analyte under given experimental conditions.

4.1.2 Applications of MESI

A hydrophobic membrane plays an important role in blocking water but allows the volatile components to permeate through and can be applied in the membrane module. Segal et al.[69] developed a system of MESI and micro gas chromatography for field analysis. After 1 min sampling time, chloroform in trap water with a concentration lower than 1ppb was detected. The sensitivity of the micro-GC system was increased by a factor of more than 100 by adding the MESI system. Liu et al.[27] applied this system to continuously monitor the air quality of a fume hood in a laboratory, chloroform in a swimming pool and toluene in a sewer pipe. Concentration profiles of these VOCs during a certain period were obtained by continuous monitoring. Biogenic emissions also were monitored by MESI-GC system.[55, 54] α-pinene, *m*-cymene, eucalyptol, limonene and *y*-terpinene were detected from the *Eucalyptus dunnii* leaves. In breath analysis, the use of MESI eliminated the need to

use the traditional sampling bags resulting in a simplification of the sampling process. In addition, a PDMS membrane prevented the moisture present in human breath from entering the sorbent trap and GC system. Trace levels of ethanol, acetone, isoprene, ethylene have been analyzed in breath samples.[64, 29, 39]

4.2 Components of MESI

4.2.1 Membrane module

The membrane, which performs a separation function, is the most important component in the MESI system. It is highly selective of analytes because each type of membrane material has its own permeability for the specific analyte. The selection of the membrane should be carefully taken into account. Previous work indicated polydimethylsiloxane (PDMS) is the most effective and widely used membrane. It allows a variety of non-polar organic compounds to permeate from air and aqueous matrices rapidly and efficiently due to the high rate of diffusion.[70] Moreover, a PDMS membrane is physically and chemically stable up to 400°C.[71] In addition, a PDMS membrane can block water from permeating through; therefore, it can be immersed in water and remains dry on the inside during sampling if the membrane module is gastight.

The construction of the membrane module is shown in Figure 4.3[29]. A piece of the membrane sheet is inserted between the two Teflon spacers in the membrane module. These two Teflon spacers are also sandwiched between two stainless steel sheets. Both the upper Teflon spacer and the upper steel sheet have two holes which are matched and allow the carrier gas to pass through. The lower Teflon spacer has a u-shaped channel to match

the channel that is cut into the lower steel sheet. The pressure of carrier gas helps the membrane to expand into the u-shaped channel in the lower Teflon spacer during operation. Carrier gas passes along the channel formed, and the dimensions of the channel in the lower Teflon spacer determine the overall sizes of the channel on the receiving side of the membrane.[29] Wire mesh is fixed to the lower steel sheet to support the membrane and prevent it from breaking when carrier gas is traveling along the u-shaped channel. The module is sealed tightly by using 12 screws to fasten the two steel plates together.

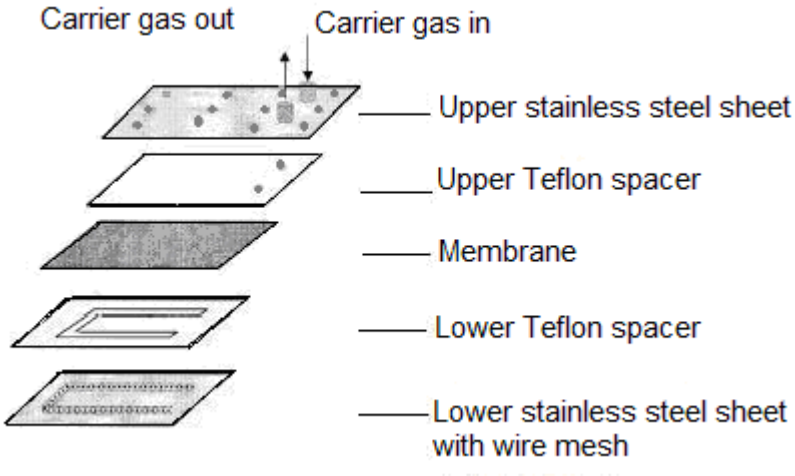


Figure 4.3 Schematic of membrane module[29].

4.2.2 Sorbent interface

The sorbent interface is another important section in the whole MESI system. The most important function of a sorbent interface is to preconcentrate the analyte of interest which is usually present at a very low concentration. The sorbent interface is made up of a sorbent trap and a heating and cooling unit. The sorbent trap shown in Figure 4.4 is simply made of a stainless steel tube by packing with a sorbent material, fixed in expected position by two stainless steel spring stoppers. Analytes extracted by the membrane are delivered by

the carrier gas to the sorbent trap and preconcentrated there until a sufficient amount is adsorbed. The trapped analytes are desorbed thermally and swept by the carrier gas into the instrument.

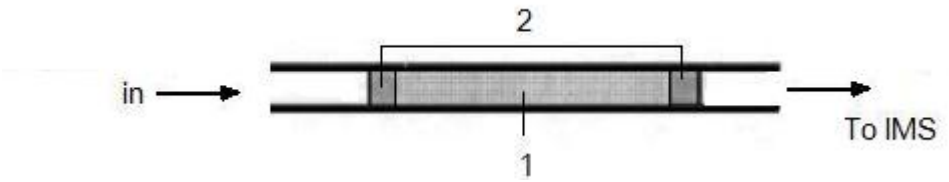


Figure 4.4 Schematic of sorbent trap (1) sorbent material; (2) stainless steel spring stoppers.

Selection of the sorbent material is dependent on the chemical and physical properties of the analytes of interest. Polydimethylsiloxane (PDMS), divinylbenzene (DVB), Tenax TA or Carboxen are widely used as sorbents in the research of MESI.[71] PDMS is silicon-based organic polymer. The non-polarity of PDMS makes it perfect for trapping non-polar analytes. DVB, a hydrophobic crosslinked polystyrene copolymer resin, has a chemically homogeneous, nonionic structure with large surface area, due to its primarily mesoporous structure. DVB is used to adsorb semi-volatile compounds.[72] Tenax TA is a porous polymer that was designed to adsorb volatile and semi-volatile compounds. It is widely used as a sorbent due to its relative non-reactivity with most organic pollutants[73] and its high thermal stability, generally up to 450°C, which allows for the trapping and desorption of organic compounds with high boiling points. Carboxen is a carbon molecular sieve designed for the analysis of light hydrocarbons.[71] Silica gel is granular, porous form of silica with a large surface area of approximately 800 m^2/g.

The temperature of the sorbent trap is an important factor that can affect the

absorption and adsorption efficiency. Decreasing the sorbent temperature can increase the performance of sorbent trapping efficient. At low temperatures, typically below 0 °C, the analyte partition coefficients between the sorbent and gas are often several orders of magnitude higher than at room temperature.[74] A high temperature will shorten the desortpion time, however, it also will affect the recovery of sorbent material. Therefore, temperature applied to the sorbent trap should be selected carefully in accordance with the properties of both sorbent material and analytes.

4.3 Experimental

4.3.1 Materials and supplies

α-pinene (analytical grade) was purchased from Sigma-Aldrich (Oakville, ON, Canada). Nitrogen (5.0 ultra high purity, 99.999%) was purchased from Praxair (Kitchener, ON, Canada). Silica gel (grade 12, 60/80 mesh) was purchased from Supelco. Stainless steel hypotubings, 19 gauge, were purchased from Small Parts Inc. (FL, US). Flat sheet PDMS membrane (SSP-M823, 0.005") was obtained from Silicone Specialty Products Inc. (Ballston Spa, NY, US). A living branch from a peppermint plant was monitored on-site.

4.3.2 MESI device construction

The details regarding the construction of the membrane module and MESI system were described previously.[29] For the current study a piece of membrane (3.8 cm x 2.6 cm) was mounted into a module. The membrane module was immersed in de-ionized water while being purged with nitrogen gas for leak detection prior to use. An 80 mm length of

19 gauge tubing was packed with 15 mm length of silica gel sorbent to construct a sorbent trap for MESI system. The packing technique for the sorbent trap was the same as that described previously for NTDs.

4.3.3 Instrumentation

A Sabre 2000 ion mobility spectrometer, obtained from Smiths Detection (Mississauga, ON, Canada) equipped with ^{63}Ni ionization source and was programmed in the positive mode using water as the calibrant/reactant ion. The IMS was operated with a drift tube temperature of 111 °C. The inlet temperature was set to 200 °C. The spectra were collected after a 0.1 s delay with a shutter grid width of 0.2 ms. The analysis duration was set to 30 s.

The thermal desorption (TD) unit was described in Chapter 2. But for MESI study, the pulse was directly applied on the sorbent trap, instead of the disrober/transfer line used in SPME and NTD studies. After sampling, the sorbent trap was then heated rapidly using a power supply. Figure 4.5 shows the photograph of the instrument interface setup for MESI-IMS.

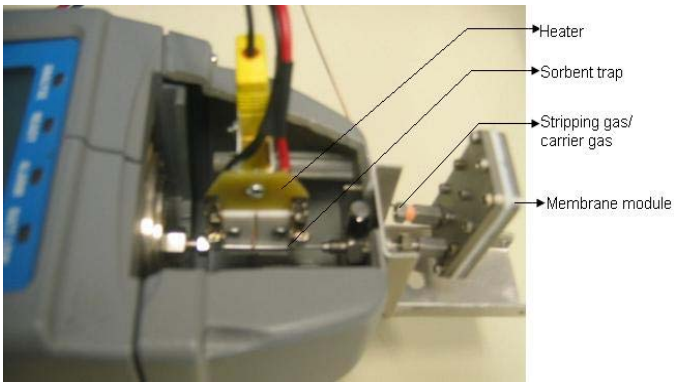


Figure 4.5 Instrument interface setup for MESI-IMS.

4.3.4 Standard gas generation

A homemade permeation tube was kept at room temperature (24 °C) to produce α-pinene standard gas flow, which was induced into a 250 mL glass sample chamber, designed and constructed at the University of Waterloo Science Shop. The flow rate was monitored by a flow meter manufactured by J&W Scientific (Flosom, CA, US) and was varied to provide different α-pinene concentrations when needed. The α-pinene concentration was calculated based on permeation rate (1263 ng/min) and total flow rate.

4.3.5 Sampling by MESI

The membrane module was placed in a 250 mL glass sampling chamber for a steady state, extraction time profile, desorption temperature, stripping side flow rate and calibration experiments. The schematic of MESI system for experimental studies is illustrated in Figure 4.6. In on-site sampling, a branch of a peppermint was enclosed in a plastic bottle with a hole on one side, into which the membrane module was fitted for directly sampling the emissions in the bottle. A sampling time of 20 min was used for on-site sampling.

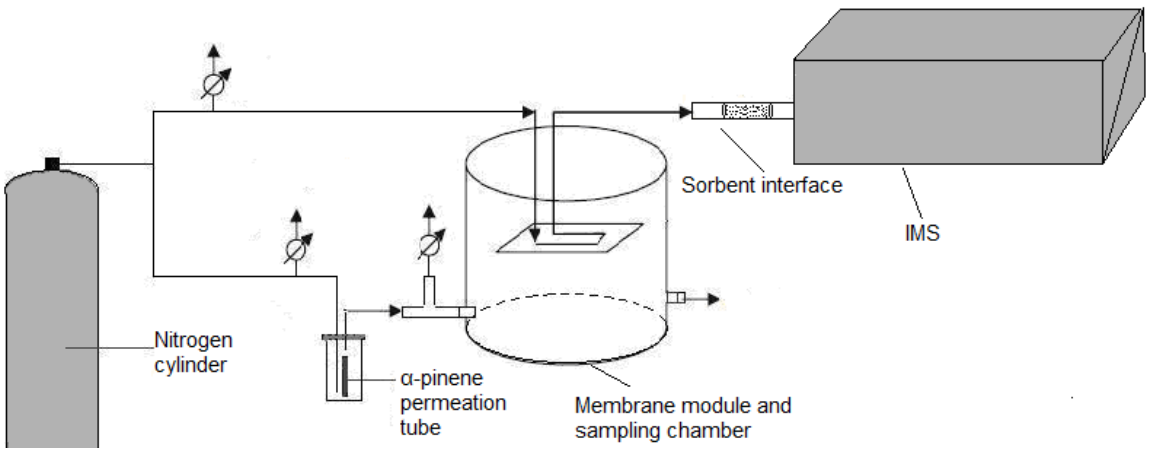


Figure 4.6 Schematic of MESI system for experimental study.

4.4 Results and discussion

4.4.1 Study on steady state

A steady state is a situation in which all state variables are constant. Steady state is an important parameter in MESI. Once a target analyte is introduced into the MESI sample chamber, it takes time for the analyte to permeate through the membrane. Since MESI allows continuous monitoring and many desorption are available, it is necessary to know if the system is under the steady state situation. Only the peaks obtained under the steady state situation can accurately represent the analyte passing through the membrane. Consequently, these peaks are useful for data analysis.

For the steady state experiment, α-pinene was introduced into the sampling chamber. The desorption temperature was increased to 280°C immediately. The results in Figure 4.7 illustrate that the α-pinene peaks become constant after 35 minutes of permeation. That meant a 35-min-permeation time is enough to reach steady state for α-pinene. Therefore, for quantitation purposes, data should be taken after 35 minutes.

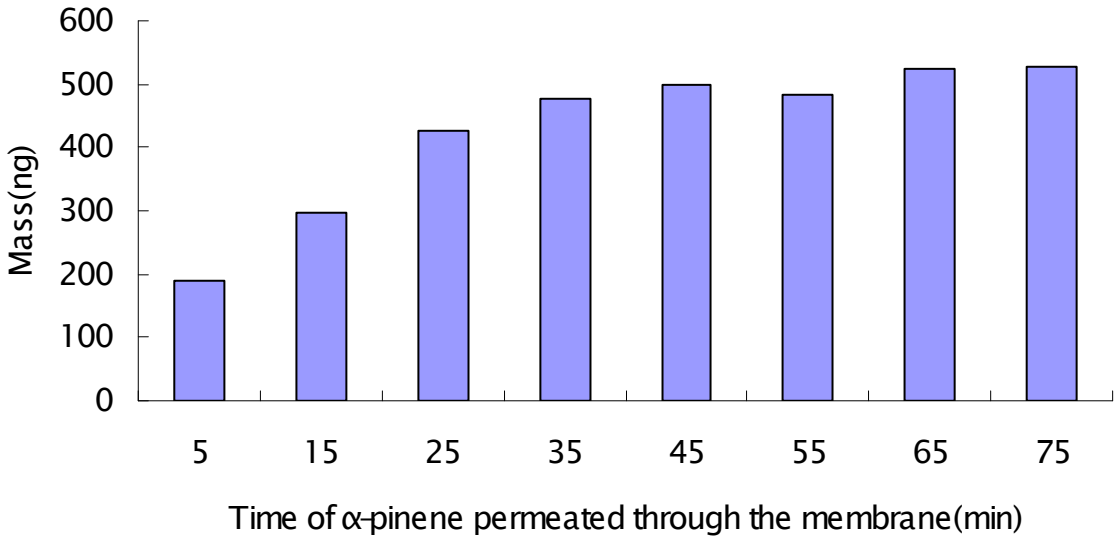


Figure 4.7 Effect of time of α-pinene permeated through the membrane on trapping efficiency. Concentration of α-pinene: 50ng/mL, trapping time: 5min, flow rate of stripping side: 10mL/min, desorption temperature: 280°C

4.4.2 Desorption temperature

α-pinene has a relatively high boiling point and affinity for silica gel sorbent, so the system should exhibit carryover without a suitable desorption temperature. Figure 4.8 shows the results of desorption temperature profile obtained from averages of three repetitions with R.S.D. values between 4 and 14%. The response of α-pinene did not change significantly when the desorption temperature raised from 200°C to 250°C. The response increased 10% when the desorption temperature was increased to 280°C. As expected, the carryover of analyte also decreased considerably at higher temperatures. A desorption temperature of 280°C and 250°C could exhibit approximately 16% carryover while a desorption temperature of 250°C had 19% carryover. Thus, a desorption

temperature of 280°C was selected for this study. Since one run only took 30 sec, a cleaning step was used to ensure no carryover of analytes in the sorbent materials after each analysis.

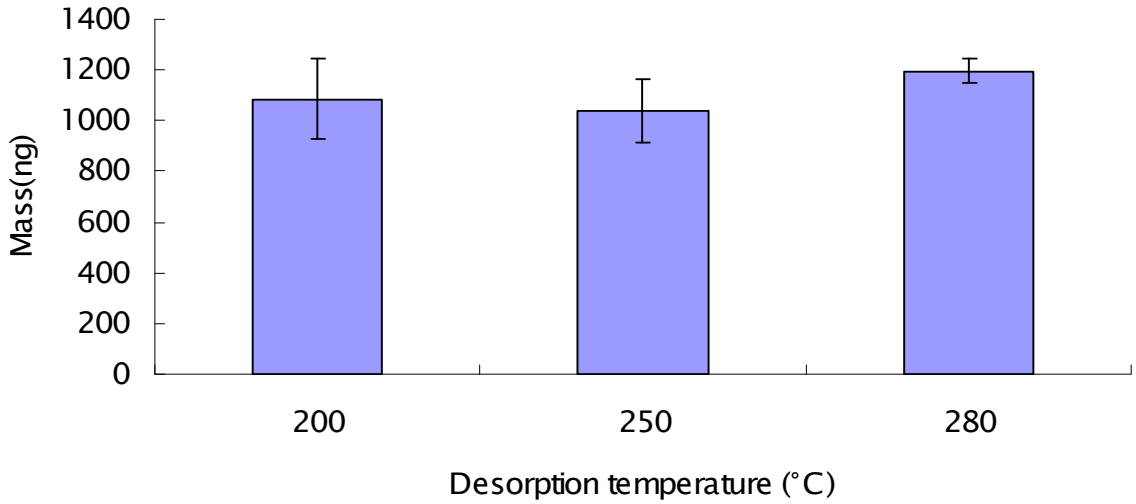


Figure 4.8 Effect of desorption temperature on desorption efficiency of α-pinene. Concentration of α-pinene: 50 ng/mL, trapping time: 10min, flow rate of stripping side: 10 mL/min.

4.4.3 Trapping time

In MESI, analytes permeate through the membrane and are trapped by the sorbent trap for a certain time, after which they are thermally desorbed. Based on Eq. (4.1), the trapped amount of analytes is expected to be proportional to the trapping time before the breakthrough of analytes.

An average of three peaks was used to create the trapping time profile shown in Figure 4.9. The results show an increase in α-pinene signal from 2 minutes to about 25 minutes of analyte accumulation with R.S.D. values between 6 and 16%. After 10 minutes,

however, the extraction amount of α-pinene increased slowly, likely as a result of breakthrough. These results suggest that a trapping time of 10 minutes is sufficient for a maximum amount of α-pinene to accumulate in the trap.

For 50 ng/mL of α-pinene**,** a trapping time beyond 10 minutes will result in breakthrough, because the sorbent material already reaches its maximum extraction ability and is unable to retain anymore analyte. In general, a short sampling time can be obtained for high-concentration applications, while for low concentration samples the sampling time can be extended to maximize the response for the target analytes.

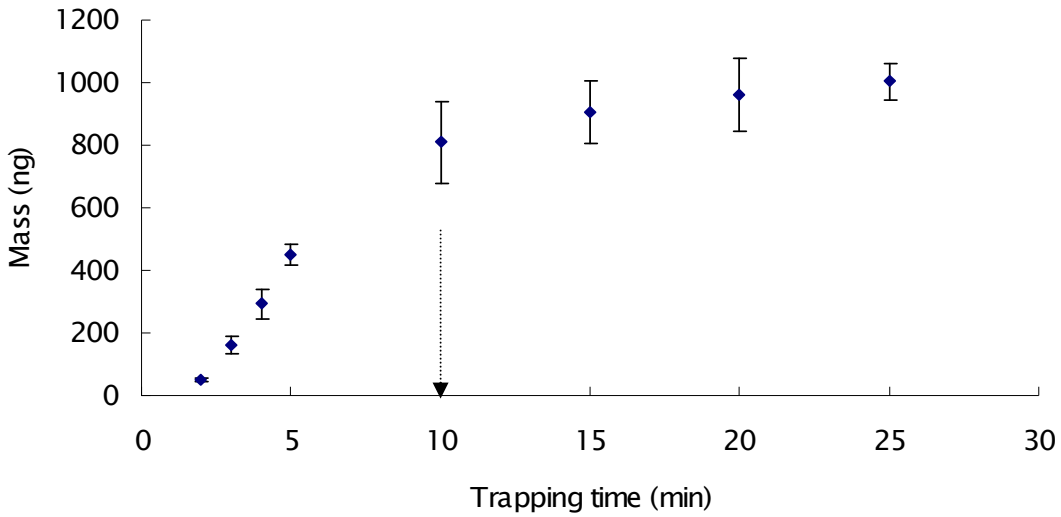


Figure 4.9 Effect of trapping time on the extraction efficiency of α-pinene with a concentration of 50 ng/mL.

4.4.4 Study on breakthrough

Breakthrough occurs when the sorbent materials cannot retain more analytes because the amount of sorbent material is insufficient to trap the total amount of analytes. Breakthrough causes a loss of analyte, resulting in experimental results that cannot reflect

the actual information pertaining to the analyte. To test the capacity of the sorbent, a second sorbent tube was connected in series to the original sorbent trap in connection with the membrane module as shown in Figure 4.10. The target analyte was brought in by the carrier gas from the sampling chamber to the sorbent trap first. When breakthrough happened, the extra analyte went into the left side trap since it could not be trapped by the first trap. After a certain trapping time, the right side trap was disconnected from the line and the carrier gas was directed introduced into the left side trap. Analysis was performed by increasing the desorption temperature on the left side trap from room temperature to 280^{o}C.

The results of this test show that trapping at 15 minutes, a little bit longer than 10 min from the trapping time study, caused breakthrough. According to the trapping time study, even after 10 min trapping, the signal of α-pinene was still increased. It meant the concentration of α-pinene downstream of the right side trap was lower than that of the upstream of the same trap. In addition, even 15 minutes of trapping time was applied to the right side trap, which was longer than 10 minutes breakthrough time, but the left side trap only had extracted the extra analyte that came from the first trap for 5 minutes. So the amount of the analyte extracted by the second trap was very small and hard to be detected. It is the reason that a longer breakthrough time was obtained by this study.

Figure 4.10 Schematic illustrating the two sorbent traps connected in series for breakthrough determination.

4.4.5 Effect of stripping gas flow rate

The stripping gas flow rate affects the thickness of the boundary layer of the inside membrane. A high flow rate will increase the concentration gradient between the outer and inner surfaces of the membrane and lead to higher permeability of analytes. But at the same time, a high flow rate may shorten the breakthrough time of the sorbent trap and decrease its extraction efficiency. In this study, the enrichment of analyte was increased concurrently with the flow rate. Flow rates of the stripping side were increased from 4.5 to 10.0 mL/ min, the signal intensity of α-pinene increased 68%. However, with the flow rate of stripping gas increased from 10.0 mL/min to 14.0 mL/min, the signal of α-pinene increased 19% only. The reason is the effect of the boundary layer on the permeability of α-pinene was reduced after a certain flow rate of stripping gas or breakthrough occurred. In addition, if a high flow rate was applied, it would consume more nitrogen and reduce the continuous operation capability of this system.

4.4.6 System calibration

An average of three repetitions was used for each of the five concentration values to create the external calibration curve for α-pinene. The modified calibration curve was constructed by removing an offset of 18.4 digit unit from the data. The calibration curve illustrated in Figure 4.11 shows good linearity. α-pinene was linear from 6.8 ng/mL to 63.3ng/mL. ($y=0.9608x$, $R^2= 0.9819$) The R.S.D. values were between 4 and 12%. Detection limit, measured on basis of S/N=3, was 2.3 ng/mL.

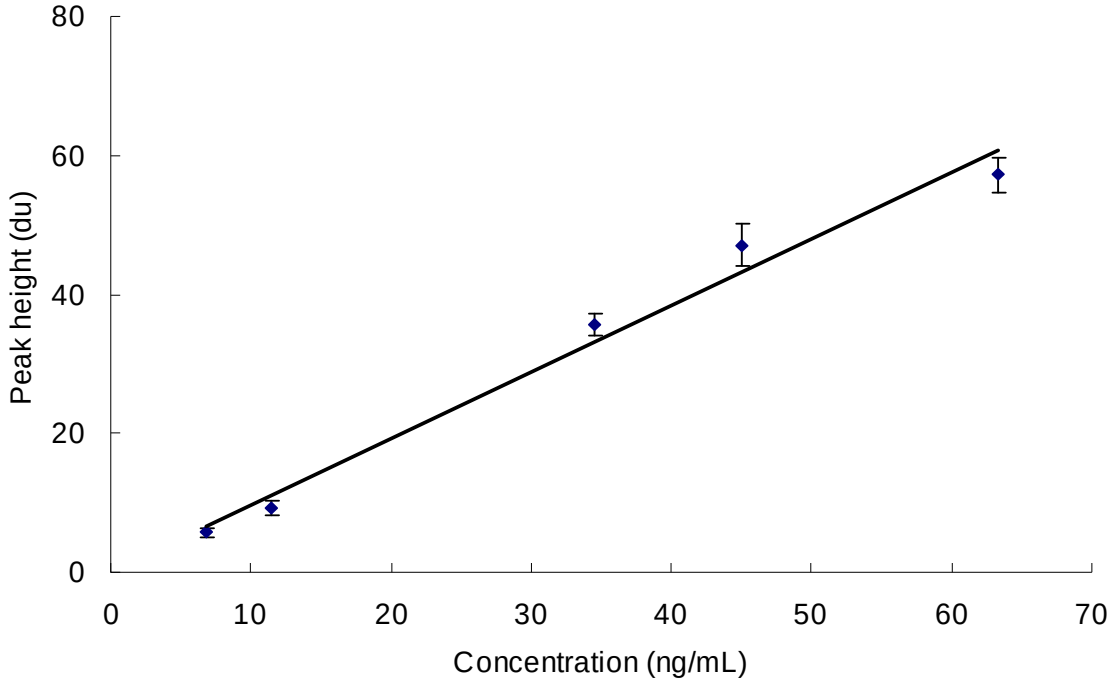


Figure 4. 11 Calibration curve for α-pinene.

4.4.7 Monitoring α-pinene emission from peppermint

As Figure 4.12 shows, α-pinene emission from the leaves of peppermint fluctuated as the sampling day progressed. Since both temperature and light are the main factors to influence biogenic emission.[75] We can see the emission peak reached a maximum level at 17:50 when the temperature was the highest in the sampling day. The emission peaks decreased as the temperature decreased and sunshine was blocked by the neighbour building. It is suggested that the variation of α-pinene emission is a result of the variations of solar radiation and temperature conditions during the sampling days.

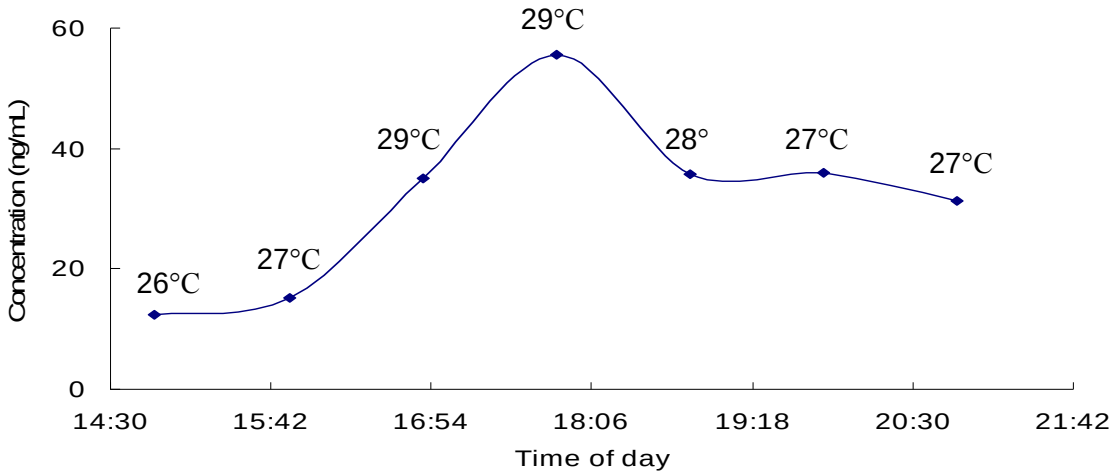


Figure 4.12 Profiles of α-pinene emitted from a branch of a peppermint in 6 hours.

4.5 Conclusion

The MESI-IMS system described herein has been shown to be a very versatile method for continuous, on-site, and reliable environmental monitoring. This system combines sample real-time extraction, preconcentration, and sample introduction in one step, eliminating the steps in sample preparation that are the main source of sample loss and contamination.

The system was optimized for the analysis of the important biogenic emission, α-pinene. The MESI system was examined for steady state, breakthrough, desortpion temperature, trapping time using standard α-pinene. The MESI-IMS system successfully detected and quantified α-pinene emitted from peppermint though a day.

With further study on membrane and sorbent materials, this system can be applied to other environmental on-site measurements. New application areas include monitoring emerging contaminants, biological samples, and less volatile and more polar compounds.

Chapter 5. Summary

Three solvent-free sample preparation techniques, SPME, NTD and MESI, were coupled to a portable IMS equipment with a thermal desorption unit. These analysis systems combine sample real-time or near real-time extraction, preconcentraion, and sample introduction in one step, avoiding the loss of sample and contamination. They provide the ability of on-site monitoring of VOCs in different sources.

In this research, SPME-IMS, NTD-IMS and MESI-IMS systems were constructed. Experiments were performed to investigate carrier gas flow rate, desorption temperature, and extraction time/volume for target analytes in different systems. These three analytical systems were successfully applied to monitor VOCs in different sources on-site. Variations of acetone level in human breath before and after taking food were monitored by SPME-IMS system. α-pinene emitted from plants, was monitored with NTD-IMS and MESI-IMS systems. All these applications demonstrate that these systems have the advantages of small size, simple operation, fast and/or on-line sampling, rapid analysis. Further efforts should be made to investigate more appropriate coatings for SPME and sorbents for NTD and MESI to monitor a greater range of VOCs. These systems can be extended for border safety control and on-site environmental measurements.

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