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TERPENES AND TERPENOIDS DETERMINATION IN PRESENT OF OZONE BY SPME AND GC-MS

by

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A Thesis

Submitted in Partial Fulfillment of the Requirements for the

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TITLE: TERPENES AND TERPENOIDS DETERMINATION IN PRESENT OF OZONE BY SPME AND GC-MS

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Particulate matter air pollution demonstrates adverse human health effect and is one of reasons for the climate change. Monoterpenes are a class of volatile organic compounds (VOCs), which are often present in household products. They can be produced by a variety of plants and belong to biogenic VOC (BVOC) class. Due to the fact that monoterpenes often contain one or more unsaturated carbon-carbon double bonds, they can readily react with ozone, and some of the products form PM. In order to address the potential health problems caused by the use of household products, climate change, and health effects caused by BVOC emissions, an efficient, precise, accurate and environmental friendly analytical sampling and detection method needs to be developed. In this work, a dynamic solid phase microextraction (SPME) sampling method is coupled with gas chromatography (GC)/mass spectroscopy detection for both single monoterpene and complex monoterpene mixture analysis in the presence of ozone. Not only the effects of parameters such temperature, pressure and relative humidity need to be known, but also how the sampling time, flow rate, ozone concentration and monoterpene type affects this analysis method are needed. In consideration of the difference between reactive monoterpenes and nonreactive monoterpenes, several single monoterpenes were selected and smog chamber experiments were conducted. The precision of the sampling method at various sampling times, flow rates and ozone concentrations were compared for both single monoterpenes and monoterpenes mixture. The sampling flow rate had no significant effect on this SPME sampling method. On the contrary, the GC response did have noticeable change when the sampling time

and the ozone concentration were varied. A radical scavenger study was conducted and the result indicated that radical scavenger did not have a significant effect on SPME fiber or the precision and accuracy of sampling method.

DEDICATION

I would like to dedicate this thesis to my mother and father who financially and emotionally supported me throughout this endeavor.

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CHAPTER 1

INTRODUCTION

1.1Particulate Matter

Particulate matter (PM) is a complex mixture of small particles and liquid drops suspended in a gas, including inorganic salts, organic compounds, dust, metals, and water. Particulate matter has a wide size range, from tens to hundreds of micrometers to nanometer molecular dimensions. [1] Particulate matter is the most visible and obvious form of air pollution. Solid or liquid particles suspended in air are often referred to as aerosol. Atmospheric aerosol can be released from both anthropogenic and natural sources. The anthropogenic sources include but are not limited to industrial activities, the burning of fossil fuels by motorized vehicles, and tobacco smoke. The natural sources include aerosolized sea salt, volcanic eruptions, forest and grassland fires, and the reaction products of oxidants with biogenic VOCs emitted from vegetation. Due to the varied sources, the chemical composition of aerosol is complex, and it is difficult understand the impact of atmospheric aerosol on human health, visibility, and climate change.[2-7]

Atmospheric particulate matter is often characterized based on particle diameter. Particles with diameters smaller than 0.1 μm are nucleation mode particles. Accumulation mode particles are larger than nucleation mode particles and the diameters range from 0.1 μm to 2.5 μm. Particles with diameters larger than 2.5 μm are termed coarse mode particles. [8] The diameter of a particle affects the particle's settling velocity, which is the rate that suspended particles deposit due to gravity. Particles with larger diameter have larger settling velocities, and particles larger than 10 μm have a relatively small suspension life-time and can be easily filtered out by human

nose and upper airway. Particles with diameters smaller than 10 μm have significant adverse effects on human health, atmospheric visibility, and climate. Due to these adverse effects, the US EPA sets standards for ambient particulate matter concentrations.[9]

1.2 Monoterpenes, terpenoids, and Household Products

Atmospheric oxidation of monoterpenes and terpenoids contributes to formation of particulate matter. The terpenoids are the chemicals that modified from terpenes, by oxidation or rearrangement of the carbon skeleton. In some literature, the authors use terpenes to include all the terpenoids. One terpenoid selected in this study was isobornyl acetate, which can be derived from alpha-pinene. Monoterpenes are a class of organic compounds that consist of two isoprene units. They have the molecular formula of $C_{10}H_{16}$, and usually contain one or more unsaturated carbon-carbon double bond. Monoterpenes with carbon-carbon double bonds can react with atmospheric oxidizing agents, such as ozone and hydroxyl radical.[10] Monoterpenes can be produced by a variety of plants, especially from conifers.[11] Moreover, they also can be emitted from some insects such as termites or swallowtail butterflies through their osmeteria.[12] Artificial synthesis can also be one way to produce monoterpenes.

One of the most distinguishing characteristics of a monoterpene is that it often has a strong odor, which sometimes accompany a protective function.[13] Monoterpenes are widely used in household products, such as air fresheners, glass and surface cleaners, and disinfectants. For example, limonene has been used as an ingredient in floor wax, room freshener, detergent, all purpose-cleaner, glass and surface cleaner, and antibacterial spray.[14] Singer et al. showed that high terpene concentrations can occur by using some consumer cleaning agents. Typical indoor concentrations of monoterpenes from the use of household products can reach ppb levels. For example, over a 5 hour period of plug-in scented-oil air freshener use, the range of VOC

concentrations ranged from 2.7 to 16.7 ppb. The use of a general-purpose pine oil-based cleaner to mop the floor gave a range of VOC concentrations from 1 ppb to 166 ppb.[15] Other monoterpenes, such as 3-carene, α-pinene, and β-pinene are also present in household products and contribute to VOC concentrations.[16, 17]

1.3Monoterpenes and Ozone

The indoor environment provides good potential for the gas-phase reaction of various chemical substances present in household products with oxidants. Indoor chemistry is one of the main sources of indoor PM. Ozone and monoterpenes are commonly found in indoor environment. Air monitoring in schools, hospitals, offices, and restaurants showed the typical monoterpene concentrations ranged from 2 ppb to 98 ppb.[12] EPA data show that the average ambient ozone concentration at 2010 was 72 ppb. [18] There are several factors can affect the indoor ozone concentration, and the transfer between indoor ozone and outdoor ozone is significant. Indoor ozone levels were usually 30% to 70% of the outdoor ozone concentration levels. [19] The unsaturated carbon-carbon double bond(s) in monoterpenes can readily react with ozone, and the some of the products to form and/or contribute to PM. Recent attention to indoor PM formation has emphasized the monoterpenes and ozone reaction as a source of particulate matter in the indoor environment.[20] Weschler indicated that the indoor air quality may be significantly impacted by the reaction of monoterpenes with ozone and/or hydroxyl radicals in indoor air.[21] Various ozonolysis products have been found indoors, such as limonon aldehyde, ketolimononic acid, limononic acid, 5-hydroxy limononic acid, 7-hydroxy limononic acid, and limonalic acid.[22, 23, 24]

1.4Particulate Matter and Human Health

Even though some correlations between poor air quality and adverse human health effects

have been realized since civilization's antiquity,[25] the worldwide concern for the adverse human health effects from air pollution began in the twentieth century,[26] when several severe air pollution events occurred. For example, in 1930, the Meuse Valley fog killed 60 people and thousands of people were suffered with pulmonary symptoms in Belgium.[27] Twenty years later, the Great Smog of '52 affected London over five days in December. During this smog episode, an estimated 4,000 people died prematurely and 100,000 people became ill because of the smog's effects on the human respiratory tract.[28] Due to the impact of air pollution on human health, air pollution research and regulation has increased, with focus on particulate matter.[29] PM is a made up by extremely small particles and liquid droplets, which can be easily inhaled and transfer into blood steam, thus PM has adverse effects on human health. For example, the Harvard Six Cities Study, which followed 8,111 patients for 16-18 years, demonstrated that cities with higher particulate matter levels had a higher adjusted mortality rate than the less polluted cities.[30] PM contributes to cardiovascular, cerebrovascular, and respiratory disease.[31] PM has long-term exposure effects, such as chronic bronchitis, and short-term exposure effects, such as asthma symptoms. [32-34] A dose-based PM and human disease relationship has also been demonstrated.[35]

1.5 Particulate Matter and Climate

Climate change can occur when the distribution between incoming solar and outgoing terrestrial radiation in the atmosphere is altered. The energy balance between incoming and outgoing radiation is termed radiative forcing (RF)[28] and is quantified as watts per square meter. A positive RF value tends to cause the climate to warm, while a negative RF causes the climate to cool. For example, increases in CO_2 and other greenhouse gas emissions reduce outgoing solar radiation, and these are considered positive RFs.

Through direct effect, indirect effect, and semi-direct effect, atmospheric PM impacts climate by altering the Earth's radiative balance between incoming and outgoing radiation.[36] The direct effect describes PM that scatters and absorbs shortwave and longwave radiation. The direct effect is a negative radiative forcing, meaning that it tends to cool the Earth's surface.[37] PM also impacts climate via the indirect effect, a negative radiative forcing, because PM modifies the microphysics of clouds. The first indirect (or Twomey) effect considers the impact of PM on the number of cloud droplets, which leads to increased radiation scattering and, in turn, negative radiative forcing. The second indirect (or Albrecht) effect is caused by PM that modifies a cloud by dividing a fixed amount of water into smaller droplets, which decreases precipitation and increases the lifetime of the cloud. [38] In addition to these direct and indirect effects, PM absorption of radiation can alter the temperature structure of atmosphere and changes cloud coverage, which is called semi-direct effect.[39]

1.6 Secondary Organic Aerosol and Chamber Study

The atmosphere is a complex environment, and multiple reactive VOCs which are precursors for PM exist in the atmosphere simultaneously. The reaction of VOCs with oxidants are a significant source of secondary organic aerosols (SOA) in atmosphere.[40] The generated SOA contributes to PM concentrations both indoors and in the atmosphere, and as a result, SOA formation is linked with air quality, visibility, public health, and climate. Therefore, the simulation experiment of SOA formation inside the chamber improves understanding about SOA formation and the effects on air quality, visibility, public health, and climate change. Secondary organic aerosol is composed of VOC oxidation products which are semivolatile under typical atmospheric and indoor conditions. Understanding partitioning between the gas-phase and condensed-phase oxidation products is critical to predicting the aerosol yield from VOCs.[41, 42]

Thus, direct measurements of the concentrations of VOCs in a smog chamber for the SOA formation experiment are needed. The two major methods for VOC analysis in a chamber are denuder sampling and proton-transfer reaction mass spectrometry (PTRMS)[43]. Denuder sampling involves exposing the chamber air to a sorbent, often Tenax, for example, and then extracting the sorbent with organic solvents or thermal desorption followed by analysis, usually by GC/MS.[44, 45] This analytical method can determine a suite of VOCs simultaneously, but it suffers from poor time resolution, because one needs to collect sufficient sample for detection, often requiring long sampling times. Furthermore, sampler preparation and denuder clean up is time- and reagent-consuming. Thus, it loses the opportunity to measure the change in VOC concentrations during SOA formation. The PTRMS instrument offers excellent time resolution of order of minutes and detection limits of order of ppt, but it cannot distinguish between monoterpene isomers. Besides the isomer problem, cost is another reason for PTRMS not to be a good choice. The PTRMS is a $90,000 instrument, which is at least $20,000 more than the cost of SPME with an existing GC/MS instrument. The goal of this study is to overcome the problems mentioned above, time and reagent consuming, poor time resolution, and expensive instrument.

1.7 Solid Phase Microextraction Sampling Method

Solid phase microextraction (SPME) is a sampling and sample preparation method that was introduced in the late 20th century.[46] There are four major advantages of SPME in comparison to other sampling techniques. First, SPME combines sampling, isolation, and enrichment into one step.[47] Second, in contrast to traditional sampling preparation methods which require the use of organic solvents, SPME rarely needs organic solvents to absorb and desorb analytes.[48] This reduces hazardous waste generation. Third, a single SPME fiber can typically be re-used for dozens of times to hundreds of times, even thousands times under some

circumstances. The reusability of the SPME combined with the reduced need for organic solvents makes SPME an economical sampling method. Last, SPME includes a wide range of sampling applications, including environmental, food, forensic, pharmaceutical, and clinic analysis. For example, Zhou et al. used SPME with headspace extraction method to sample phenols in aquatic samples.[49] SPME sampling is not limited in aquatic samples, but it also can collect gas phase samples and from the headspace of solid samples. In 2004, Navalon et al. used SPME to extract fungicides from soil samples.[50] According to the ISI Web of Knowledge record,[51] between 2000 and 2013, 999 of the 12,094 SPME publication were related to environmental applications. Also, the SPME sampling is not limited to on-site immediate analysis, but off-site analysis as well, due to the fact that the SPME fiber can be withdrawn to the SPME holder and transferred to laboratory for later analysis. For example, SPME has been used to sample volatile organic compounds in indoor air coupled with GCMS analysis.[51]

To date, there are several commercially available SPME fiber coatings that select for the different target analytes and sample matrixes: polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), carboxen (CAR), and carbowax (CW). SPME fiber coatings are available with different thicknesses, which affect the fiber lifetime, durability, and reproducibility of the extraction.[52] It is critical to choose the appropriate fiber for the certain application.

In addition to the SPME fiber coating type, the sampling time is another factor that affects the precision and accuracy of SPME sampling methods. The operating principle of SPME sampling is that distribution equilibrium between the analyte in the matrix and analyte absorbed on the fiber occurs. When the system reaches the equilibration time, the amount of analyte extracted from the matrix remains the constant. Therefore, when the system is under stationary

conditions, the amount of analyte absorbed by the fiber is not related to the variation of mass transfer. However, when target analytes are extracted from liquid by headspace method, a very slow increase will follow the rapid extraction time curve, because the target analytes need transport to headspace from liquid to gas phase before they reach the SPME fiber.[43]

Target analytes in samples are often sampled using static SPME. However, one of the drawbacks of static SPME sampling is that it requires a relatively long sampling time, up to two hours. This increases the time resolution between samples. Dynamic SPME sampling overcomes this disadvantage.[53] Dynamic SPME sampling significantly reduces the sampling time and maintains the reproducibility of sampling.

The major goal of this thesis is to provide a fast, accurate, and green sampling method for reactive gas phase terpenes in a smog chamber by using dynamic SPME with separation and detection by GCMS. The experimental setup details, the experimental parameters monitoring, SPME sampling method, and GCMS analysis method are described in the Chapter 2. In Chapter 3, the results from single VOC experiments and complex VOCs mixtures experiments are present and discussed. Meanwhile, the effect of ozone concentration, radical scavenger, sampling time, and sampling flow rate are also studied in this thesis.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Overview of Experimental Procedure for Dynamic SPME Sampling Method

For this study, the gas phase mixtures of terpenes, terpenoids, and derivatives were prepared in the SIUC 5.5 m^3 environmental smog chamber (Figure 1). The terpenes, and terpenoids, used in this study were α-pinene, limonene, 3-carene, p-cymene, borneol, α-phellandrene, and isobornyl acetate. The pressure, temperature, relative humidity (RH), particle size and number concentration, and ozone concentration were monitored by different instruments during each experiment. Because the goal of these experiments is to develop a method that can be used in secondary organic aerosol generation, in some experiments, ozone, an oxidant, and 2-butanol, a radical scavenger, were added to the chamber. Samples were collected by dynamic SPME method and analyzed by GC/MS, and the data collected from these instruments were used to optimize the SPME sampling method. The following sections describe the experiments in further details.

Several procedural steps took place in order to collect and analyze. First, a SPME fiber was conditioned in the GC/MS injection port before each sample was collected. A chromatogram of the conditioned fiber was collected after conditioning in order to verify that no carryover remained on the SPME fiber. After the VOC precursors were volatilized, added to the chamber, and stabilized, SPME samples were collected by dynamic sampling using a custom SPME sampling port. After sampling, the SPME fiber was inserted into the injection port of gas chromatography/ mass spectrometry immediately for thermal desorption and analysis. For each chamber experiment, at least 4 replicate samples were collected in order to confirm the

reproducibility of SPME-GC/MS sampling method. The detail of the chamber setup and experimental steps will be described in later sub-sections.

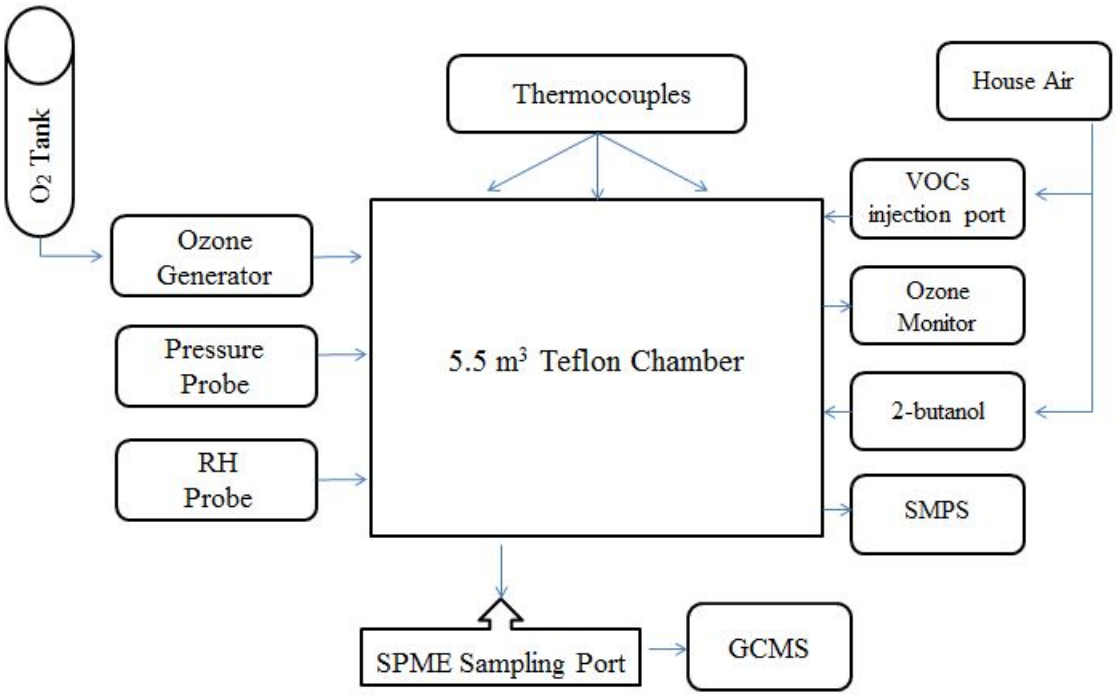

Figure 1. The complete experimental set up. The ingoing arrows indicate the ingoing gases into the chamber. The outgoing arrows indicate that gases go to the data collecting instruments.

2.2 The Experimental Smog Chamber

A 5.5 m^3 (2.5 m × 1.3 m × 1.7 m) Teflon® polytetrafluoroethylene 200 LP (nominal thickness of 50 μm) smog chamber (Welch Fluorocarbon, custom) was used to perform all the experiments. M.S. student Meagan Lynne Hatfield previously described the experimental chamber in detail.[54] The chamber was suspended from ceiling, which allowed chamber to expand and contract without strain. There was a large access hole (around 31 cm across) at the bottom of one end of the chamber, which allowed access to the inside of the chamber and helped to flush

dirty air out of the chamber. This access hole was closed during SPME sampling by wrapping the excess Teflon film over a 25 inch long ruler and secured by three binder clips. In order to reduce the risk of tears, each corner of the chamber was reinforced by polyimide Kapton film tape (McMaster-Carr, P/N 7648A715). The chamber was draped over with a blackout fabric curtain (Hobby Lobby P/N 945626) for the purpose of reducing interferences due to photo-oxidation.

There were two access ports, which were made with two sheets of polytetrafluoroethylene (PTFE) (6" × 6" × 1/2", McMaster- Carr P/N 8545K19), installed on each of the 1.3 m × 1.7 m sides of the chamber. There were eight 1/2" and six 3/8" holes drilled through each port, which were used for tubing.

For the purposes of cleaning and precursor volatilization, two in-house purified air lines (3/8" outside diameter Teflon tubing) were directly connected to the chamber via the Teflon ports with about 20 L min^{-1} flow rate. The in-house air was passed through three filters, including a carbon filter (Whatman, P/N 90408A), a silica gel desiccant filter (Fisher, P/N S684-211 and S161-212, Drierite, P/N 27068), and a high-efficiency particulate air filter (TSI, P/N 1036015). By using these three filters, the concentrations of organics, water vapor, and particles were reduced. In a typical SPME sampling experiment, the chamber was cleaned with purified air until the particle number concentration was below 1 particle cm^{-3}.

2.3 VOC Injection Port and VOCs Precursor Volatilization

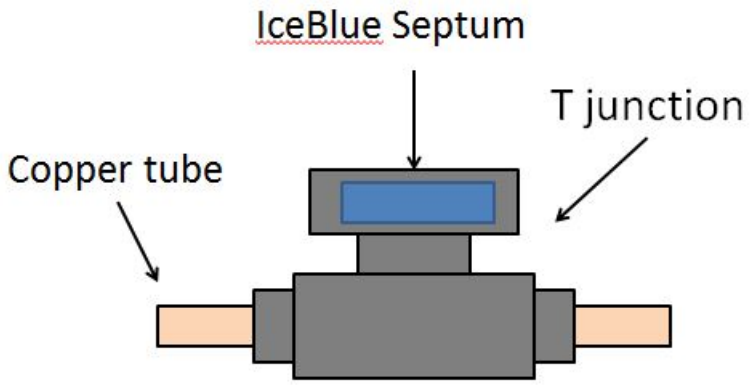

Figure 2. VOC injection port. The grey body represents Swagelok t-junction. The two ends are copper tubing The Restek Ice blue 9 mm septum is in the center of the t-junction.

The injection port was built with a ¼ inch stainless steel Swagelok t-junction with ¼ inch Swagelok connectors at either end. The injection port was connected to the smog chamber and clean house airlines with ¼" copper tubing. A Restek IceBlue 9 mm septum was placed in the center of t-junction with the back ferrule. All of the parts were cleaned by sonication under distilled water for three times, followed by a mixture of acetone and methanol solvent wash, and dried in the 120 ℃ oven overnight before each assembly.

In order to generate the gas phase VOC mixtures inside the chamber, the VOC injection port was used to volatilize a liquid VOC mixture. One end of the VOC injection port was connected with the chamber, and the other end was connected with house airline. The body of VOC injection port was wrapped by the heating tape, and 60 ^{o}C was the approximate temperature inside the port. The mixture was injected using a microliter syringe into the VOC injection port through the septum. Meanwhile, the house airline continually passed the clean

house air through the VOC injection port to the chamber for 20 minutes to completely volatilize and transfer the VOC mixture to the chamber. Then the VOC injection port was disconnected from the chamber. Five VOCs were used in this study. The detailed information of these VOCs were listed in Table 1.

Table 1:

Reagent Information

VOC	Density [g mL^{-1}][a]	Boling Point °C	Purity[a]	CAS #	Vendor
Isobornyl Acetate	0.982±0.001	231	0.97±0.01	5644-61-8	Fisher
Limonene	0.843±0.001	176	0.99±0.01	5989-27-5	Sigma
3-carene	0.864±0.001	168	0.99±0.01	498-15-7	Sigma
p-cymene	0.858±0.001	177	0.995±0.001	99-87-6	Sigma
Borneol	1.01±0.01	213	0.98±0.01	464-43-7	Sigma

[a]Errors were estimated based on the number of significant figures given by the manufacturer.

2.4 Ozone Generation and Monitoring

In order to determine the effect of ozone on the SPME sampling method, some VOC sampling experiments were conducted in the presence of ozone. An ozone generator (Azco Industries, HTU-500 AC) was used to generate ozone from oxygen gas (Airgas, ultra-high purity). The ozone concentration was recorded every 5 seconds by a Teledyne API (model 450) continuous ozone analyzer. According to the Beer-Lambert Law, the ozone concentration in the

air is directly related to the absorption of ultra-violet light at 254 nm. By comparing the absorption of UV light at 254 nm of sample air and ozone- scrubbed gas, the analyzer determined the ozone concentration in the chamber air. To assess the effect of ozone on SPME sampling, the peak areas of VOCs were measured in the presence of four different concentrations of ozone ranging from 70-1100 ppb and, for comparison, in a blank experiment, where no ozone was added to the chamber and the background ozone concentration was < 10 ppb.

When performing these SPME sampling experiments in the presence of the ozone, the terpene mixture was injected into the chamber before adding ozone, and the ozone reacted with terpene upon mixing. Therefore, the initial ozone concentrations cannot be measured. Instead, these ozone concentrations were pre-determined by chamber experiments in order to provide the accurate total ozone concentrations. To calibrate the ozone generator, the ozone generator was set to level zero and then ozone generation was initiated for a fixed time period to generate difference ozone concentrations in the chamber. In separate experiments, ozone was generated (in triplicate) for 1 min., 2 min., 4 min., and 6 min. The chamber was closed and allowed to stabilize for 1 hour. Meanwhile, the ozone analyzer sampled the chamber air at 5 second intervals. When at least 50 samples of chamber air showed agreement within 1 ppb, the ozone concentration was considered to be stable. The average ozone concentrations for 1 min., 2 min., 4 min. and 6 min. at level zero ozone generation were 73 ppb, 258 ppb, 619 ppb, and 1084 ppb. A relative standard deviation of less than 7% was typically reached. This implied that ozone generator provided a reproducible ozone source.

2.5 Experimental Parameters Monitoring

Three thermocouples (Omega, P/N SA1-K) were used to continuously monitor the temperature of the chamber. One thermocouple was adhered to the outside to each of the 1.3 m × 2.5 m sides of the chamber. The third thermocouple was adhered to the bottom of the chamber (1.7 m × 2.5 m side). In order to record the data from the thermocouples to data logging software, a high-speed USB carrier (National Instruments, P/N 192558C-01) was used. The data from the thermocouples and the data from the ozone monitor were collected and recorded into a LabView (Student edition version 8.5) program, which was programmed by undergraduate researcher, John Junge. The data were collected in five seconds intervals from the thermocouples and the ozone monitor.

The internal pressure of the chamber was measured by the Omega pressure sensor (OM-CP-PRTEMP1000SI). The Omega engineering OM-CP data logging software (version 2.00.70) was used to record the data in 5 seconds intervals.

The relative humidity and the temperature around humidity probe were measured during the entire experiment using a HUMICAP® probe (Vaisala HUMP75), which was interfaced with a Vaisala humidity meter (Model MI70). The humidity and temperature data was collected and recorded by M170 Link software (version 1.10). Air from the chamber was continuous passed through the humidity probe at flow rate of 0.3 L min^{-1}, which was supplied by the house vacuum and regulated by a flow meter (Omega P/N FL2010). A Swagelok tee (B-1610-3) that was fitted with 1 inch Teflon tubing (McMaster P/N 51805K62) was used to connect the humidity probe and the in-house vacuum to chamber. In order to reduce the interference from the outside air, Teflon tape (McMaster- Carr, P/N 7648A715) was used to wrap the probe at the tee joint part.

One end of this Swagelok setup was attached to the in-house vacuum system and the other end was attached to the chamber through a Teflon port.

2.6 Particulate Matter Concentration Monitoring

Due to the fact that the effect of particulate matter to this dynamic SPME sampling method is not known, the particulate matter concentrations were monitored during the SPME experiments. To monitor the size and number distribution of particulate matter in the chamber, a TSI scanning mobility particle sizer (SMPS, 3936), equipped with a long differential mobility analyzer (DMA, 3080) and a condensational particle counter (CPC, 3100) was used. When particles entered the SMPS, a krypton-85 (TSI model number 3077) charger provided a bipolar distribution to each particle. The charged particles entered the DMA and were separated the particles by their electrical mobilities, which is directly related to the diameters of the particles. After the particles were separated by the DMA, they entered the CPC where they were counted. The Aerosol Instrument Manager (AIM) software (version 8.0.0.0) was used to record the particles' number concentrations and diameters. For the chamber experiments performed in this study, the sheath flow was set to 3.00 L min^{-1} and the aerosol flow was set at 1.00 L min^{-1}, and the particles' diameters ranged between 13.8 nm and 749.9 nm.

2.7 SPME Sampling and Port

The dynamic SPME sampling port was composed of a 3/8 inch (95 mm) stainless steel compression tee (Swagelok, Solon, OH) as the main body (Fig. 2). A piece of Teflon tubing was inserted into the tee from the center port in order to stabilize the SPME syringe. The other ports of the tee were connected with chamber and vacuum, used as the gas inlet and outlet. A vacuum pump (Gast, P/N 0823- 1010- SG608X), provided a flow through sampling port at a rate of 5 L

min^{-1} and regulated by a flowmeter. In this study, a 75 μm PDMS/CAR SPME fiber (Supelco, 57344-U) was selected as the fiber coating. A SPME fiber holder (Supelco, 57330-U) was also purchased as a completing set of SPME sampling device.

Prior to SPME sampling, the SPME fiber was placed in the GC/MS injector port to condition the fiber. For sample collection, the SPME fiber was inserted into the central tee of the dynamic sampling port and exposed to the sample gas flow from the chamber (Fig 3). After sample collection, the SPME fiber was retracted into the sampler and then immediately injected into the injector port of the GC/MS for thermal desorption. After 5 min. desorption time, the SPME fiber was withdraw back to SPME fiber holder. The fiber was re-conditioned at GC injection port for 5 min. after the GCMS analysis program finished.

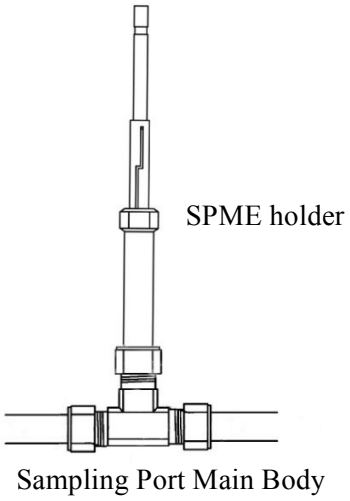

Figure 3. The dynamic SPME sampling port with SPME holder inserted in the middle.

2.8 Gas Chromatography/ Mass Spectrometry Analysis

In order to analyze the gas samples that were collected using a SPME fiber, a Saturn 2200 Varian gas chromatograph (3900)/ mass spectrometer (2100T) equipped with ion trap detector was used. A SPME deactivated glass insert liner (54 mm length × 5.0 mm o.d. × 0.8 mm

i.d., Varian) was installed. In comparison to a conventional GC insert liner, a SPME insert liner has smaller inside diameter, which can increase the linear velocity of the carrier gas, which promotes rapid introduction of the analytes onto the GC column for a narrow band. The analytes collected by the SPME fiber were desorbed in the GC injection port at 300 °C in the splitless mode for 5 min. 0.25 minutes after fiber was removed and the analysis began, the split was turned on in a 100:1 ratio. The GCMS was equipped with a Factor Four capillary column (VF-5ms, 5% diphenyl/ 95% dimethylpolysiloxane 30 m × 0.25 mm × 0.25 μm, Varian P/N CP8944).[54] The following temperature program was developed for the separation: initial temperature 50°C for 1 min, a ramp from 50 °C to 90 °C at a rate of 3 °C min^{-1}, a ramp from 90 °C to 280 °C at a rate of 45 °C min^{-1}, a hold for 2 min, with a total analysis time of 20.56 min. After separation, each analyte was detected by MS using electron impact ionization mode. The ion trap was 240 °C and scanned the mass range from 40 to 650 m/z. The manifold was held at 100 °C and the transfer line was set at 290 °C. The Varian Mass Spectrometry Workstation software (version 6.9) was used to control GC/MS instrument and analyze chromatograms. The NIST Mass Spectral Search Program equipped with the NIST/ EPA/NIH Mass Spectral Library (version 2.0d) was used as the standard mass spectrum database, which compared with each analyte in order to identify the analytes. In addition, single injections of authentic standards were also used to identify the analytes by comparing the peak retention times. To determine if previous SPME samples contained carryover analytes on the SPME fiber, blank samples were collected after analyzing each SPME sample. The GC/MS analysis results of blank samples were compared to the NIST/ EPA/ NIH Mass Spectral Library, as well as single authentic standards. At the same retention times, the GC/MS analysis results of the blank samples indicated no carryover analytes on the SPME fiber.

CHAPTER 3

RESULT AND DISCUSSION

3.1 Overview

This research aimed to investigate a dynamic solid phase microextraction sampling method coupled to GC/MS for the determination of monoterpenes in the presence of ozone. The research experiments performed under the similar indoor environmental condition, the relative humidity was between 8.00% to 11.00%, the room temperature was maintained between 21.00°C to 22.00°C, the atmosphere was kept at 1 atm, and the concentration of ozone in the smog chamber before experiment was lower than 10ppb. As a preliminary experiment, a single ozone-reactive VOC, α-pinene, was sampled using dynamic SPME in 100 L Teflon air bag and determined by GC/MS. Then, additional VOCs, including limonene, 3-carene, p-cymene, borneol, and isobornyl acetate, were sampled separately by dynamic SPME in Teflon smog chamber and determined by the same GC/MS method, separately. The results of these single VOC experiments were used as the references for comparison in the determination of VOC mixtures and to verify the effect of complex VOCs mixtures on this dynamic SPME sampling method. 2-butanol is often used as a hydroxyl radical scavenger in smog chamber experiments. Thus, the effect of 2-butanol on the sampling method was determined by comparing GC/MS peak areas of each compound collected by SPME in the presence and in the absence of 2-butanol. The sampling time and flow rate also play an important role in dynamic SPME sampling, because both factors affect the equilibrium between the analyte that remains in matrix and the analyte that absorbs on the SPME fiber. The GC/MS peak areas of each compound in the VOC mixture were compared under a range of sampling times (from 2 min to 30 min) and a

range of flow rates (from 2 L/min to 20 L/min). In order to verify the sensitivity and determine the limit of detection for this dynamic SPME sampling method, several concentrations of VOCs in a mixture were determined by this method. Since ozone is one of the most common oxidants in the atmosphere, this work also determined the effect of different ozone concentrations on the SPME sampling method. Five ozone different concentrations, from 5 ppb to 1000 ppb, were discharged into chamber after the VOCs mixture injected in the chamber. The GC/MS peak areas of each VOC compound in the mixture were compared before ozone injection and after ozone injection.

3.2 SPME Fiber Coating Selection

There are several commercially available SPME fiber coatings, such as polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), Carboxen (CAR), and Carbowax (CW). The fiber/ sample distribution constant K_{fs}, is a characteristic parameter of a coating that describes the coating's selectivity toward the analyte against other components in the matrix. Different coatings have different fiber/ sample distribution constants K_{fs}, which will impact the SPME sampling efficiency toward to different compounds[55] SPME fibers are also commercially available in different thicknesses, which affect the fiber lifetime, durability, and reproducibility of the extraction. It is critical to choose the fiber that is appropriate for each application. Recently, Spietelun et al. reviewed currently available SPME fibers coatings and the trends in SPME fiber coatings.[56] PDMS is the most often used coating to date, since it can withstand a temperature as high as 300 °C without degrading the coating, and it can be used to extract both polar and nonpolar analytes.[57] Also, for volatile compounds, mixed phase coatings are preferred to single phase coating, due to the fact that mixed phase coatings have complementary properties, leading to the higher distribution constants when compare with single

phase coating for the volatile organic compounds.[58] Therefore, in this study based on the chemical properties of our analytes, PDMS/CAR was selected as the fiber coating.

3.3 Preliminary Experiment

In order to study the use of dynamic SPME sampling as a quantitative method, a single VOC, α-pinene, was sampled, in a 100 L Teflon bag with a concentration ranging from 0.010 ppm to 1.0 ppm. Prior to the experiment, the Teflon bag was prepared by flushing five bag volumes of purified house air before injection and evaporation of α-pinene, which reduces the concentration of particulate matter and gas-phase contaminants from previous experiments. In separate experiments, 0.70 μL of liquid α-pinene were injected into the bag via microliter syringe (Hamilton, P/N 7635-01) through the VOC injection port that one end connected to the bag, one end connected to the purified house airline. The body of VOC injection port was wrapped by electric heating tape set to 60 ^{o}C , which promotes evaporation. Thus, the liquid α-pinene was evaporated and flowed into the bag, which generated 1.00 ppm α-pinene at approximately 25 ^{o}C and 1 atm inside the bag. Eight SPME samples were collected from the same bag air. The SPME fiber was exposed to the sample air for 5 min., and analyzed by GC/MS immediately. The SPME fiber was conditioned under 300 ℃ for 5 min. and cooled down before collecting the next sample. Because the tolerance of the microliter syringe, 0.070 μL α-pinene cannot be directly injected into a Teflon bag with reasonable accuracy. Therefore, in order to create a 0.10 ppm α-pinene sample, a dilution from 1.0 ppm α-pinene was done. 90% of 1 ppm α-pinene sample air was vacuumed out and refilled the bag with house air could produce 0.10 ppm α-pinene in the Teflon bag. In order to estimate when 90% of the volume of the bag obtained, the amount of time that was required to vacuum the entire bag was recorded. Therefore, the amount of time that can vacuum 90% of the Teflon bag can be calculated. 0.70 μL α-pinene was injected into the Teflon

bag, and the bag was filled with purified house air. Thus, the concentration of α-pinene inside the air bag was 1 ppm. Then, the air bag was vacuumed and 10% of the sample air remained inside the bag. After that, the Teflon bag was filled with purified house air for the same amount of the time period. The new concentration of α-pinene in the air bag was 0.10 ppm. The same dilution procedure repeated again to create 0.010 ppm α-pinene in the air bag. As the air bag didn't have any information related to the uncertainty, we estimated the absolute uncertainty was 10 L, so the percent relative uncertainty was 10%. The percent relative uncertainty of 5 μL microsyringe was 1%, therefore, the uncertainty of the α-pinene concentration was 10%.

First of all, as we can see from Table 2, the average peak area for α-pinene decreased as the concentration of α-pinene decreased in the air bag. The standard deviations of peak areas of the replicate SPME samples are a measure of the overall reproducibility of the sampling and analysis method (Table 2). The percent relative standard deviations (RSDs) range from 4% to 9%. This preliminary experiment provided foundation for the further work in smog chamber. As the results indicated, this dynamic SPME sampling method coupled with GC/MS detection is good for gas phase terpene detection and analysis without consuming laboratory time and labor. The low RSD indicates that this sampling method can provide precise result. The low sample concentration, 0.01 ppm, with good RSD, 9% relative standard deviation, suggests that this sampling method can be used for trace analyte detection in smog chamber experiments.

Table 2

Average peak area, standard deviation, and relative standard deviation of α-pinene at different concentration.

Concentration (± uncertainty)	1.0 (±10%) ppm	0.10 (±10%) ppm	0.010 (±10%) ppm
Average peak area α-pinene ±standard deviation (percent relative standard deviation) (Counts.min)	$(3.47\pm0.14)\times10^{6}$ 4%	$(9.57\pm0.64)\times10^{5}$ 7%	$(1.90\pm0.17)\times10^{5}$ 9%

3.4 SPME Sampling Method for Single Reactive VOC

The two single reactive precursors limonene and 3-carene experiments were used as the basis for comparison of the VOCs mixture studies. Limonene and 3-carene are commercially available. Limonene is commonly used in household products, as the R-(+)-isomer possesses a strong orange smell. 3-carene has sweet and pungent odor and is often used in essential oil. They were selected as reactive VOCs in this study due to their short ozonolysis half-lives, and thus these VOCs are known to react with ozone and contribute to the formation of PM within the time frame of a smog chamber experiment (4-6 hours). At room temperature, a total pressure of 1 atm, and 500 ppb of ozone, limonene has a half-life of 4 minutes and 3-carene has a half-live of 26 minutes.[59] They can rapidly react with oxidants in the atmosphere, such as ozone, to form secondary organic aerosol.

Two experiments were conducted in this study for limonene and 3-carene, individually. The first experiment was injected 8 μL limonene into the smog chamber, in term of 140 ppm limonene, and 5 SPME samples were collected from the same chamber air. The relative standard deviation (RSD) of these five single SPME samples was 10%. The second experiment was injected 8 μL 3-carene into the smog chamber, in term of 140 ppm 3-carene, and 5 SPME samples were collected from the same chamber air. The relative standard deviation of these five single SPME samples was 12%. The RSD indicated a relatively good reproducibility of this dynamic SPME sampling method.

Table 3

Average peak area, standard deviation, and relative standard deviation of Limonene and 3-Carene in smog chamber experiment.

	Limonene	3-Carene
Average peak area ±standard deviation (percent relative standard deviation)	$(9.03\pm0.86)\times10^4$ 10%	$(1.21\pm0.14)\times10^5$ 12%

3.5 SPME Sampling for Single non-reactive VOC

Several non-reactive VOCs were selected as SPME sampling method targets in order to determine the reproducibility of SPME sampling of these VOCs and to verify the effect of the presence of non-reactive VOCs on the SPME sampling of reactive VOCs. The non-reactive VOCs selected were p-cymene, α-phellandrene, eucalyptol, and isobornyl acetate. These non

reactive VOCs have good chromatographic separation from each other and reliable GC/MS peak area reproducibility. Other non-reactive VOCs, linalool and terpineol, were tested by dynamic SPME sampling. However, due to the poor GC/MS peak area reproducibility and poor peak shapes which might caused by characteristics of the SPME fiber or polarity of VOCs, they were not considered as target analytes in the VOCs mixture for the SIU Environmental Smog Chamber study.

Six experiments were conducted in this study for p-cymene, α-phellandrene, eucalyptol, isobornyl acetate, linalool, and terpineol, individually. For each experiment, 8.00 μL of each single VOC was injected into the smog chamber to give a concentration of 0.20 ppm. After mixing and stabilization of the chamber, five SPME samples were collected from the chamber by using dynamic SPME sampling method and followed by GCMS analysis. The relative standard deviation (RSD) of p-cymene, α-phellandrene, eucalyptol and isobornyl acetate were all below 20%, the relative standard deviation (RSD) of linalool and terpineol were above 20%. These target compounds are from different classes of organic compounds which mimics the possible products that can be produced in a smog chamber experiment: aromatic, terpene, acetate, terpenoid ether, and terpenoid ester, respectively. These results indicated that the dynamic SPME sampling method can be applied to various classes of organic compounds with reliable reproducibility.

Table 4

Average peak area, standard deviation, and relative standard deviation of single non-reactive VOC in smog chamber experiment.

	p-cymene (Counts-min)	Eucalyptol (Counts-min)	α-phellandrene (Counts-min)	Isobornyl acetate (Counts-min)
Average peak area ±standard deviation (percent relative standard deviation)	$(3.08\pm0.34)\times10^5$ 11%	$(4.32\pm0.38)\times10^5$ 9%	$(1.99\pm0.14)\times10^5$ 7%	$(1.06\pm0.19)\times10^6$ 18%

3.6 Low Terpenes/terpenoids Concentration Detection by Dynamic SPME Sampling Method

After establishing the reproducibility of the dynamic SPME sampling method, the combined sampling and analysis method is needed to evaluate the lowest concentration that this method can be expected to detect. The static SPME sampling method is a relatively simple method, which exposes the SPME fiber in a closed system and depense upon the equilibrium conditions. It is expected that in comparison to static sampling, the dynamic sampling is more sensitive during the same time period, since this dynamic sampling method improves mass transfer conditions by improving the likelihood that analytes diffuse to the SPME fiber. [60] The lowest concentration detected was determined by examining the GCMS peak areas of a series of terpenes/terpenoids standard mixtures. The terpenes/terpenoids mixture was made from a liquid terpenes/terpenoids stock solution consisting of 100.0 μL of 3-carene, 100.0 μL of p-cymene, 100.0 μL of limonene, 100.0 μL of isobornyl acetate, and 0.0230 g of borneol (borneol is a

solid a room temperature and pressure but dissolves in the liquid). This stock solution was used as standard mixture solution in the further experiment. Then the first dilution mixture was made by diluting 20.0 μL stock solution into 180. μL 2- butanol. The second dilution mixture was made by diluting 20.0 μL the first liquid dilution mixture into 180 μL 2- butanol by using 50 μL and 500 μL microsyringe. Four experiments were conducted in this study, 8.00 μL of liquid phase stock solution, 1.00 μL of liquid phase stock solution, 8.00 μL of the first liquid phase dilution, and 8.00 μL of the second liquid phase dilution were injected by 10 μL microsyringe and vaporized into the 5.5 m^3chamber with heating tape wrapping at the sample injection port. The mixtures were evaporated and flowed into the chamber as gas phase. In terms of gas-phase concentration of each component, they were 0.757 ppb in stock solution, 75.7 ppt in the first dilution, and 7.57 ppt in the second dilution. These concentrations are calculated as volume by volume instead of mass by mass. Four SPME samples were collected at each concentration level.

The responses of GC/MS to the amount of 3-carene, p-cymene, limonene, borneol, and isobornyl acetate at different concentration levels that extracted by this dynamic SPME sampling method were shown in Table. 5, with R^2 values. The R^2 values ranged between 0.98 and 0.99, which were deemed acceptable for use in quantification. The reproducibility of 3-carene, p-cymene, limonene, and borneol, was similar from 760 ppt level to 8 ppt level: the RSD of each component at four concentrations were $\leq$ 15%, except for limonene at 75.7 ppt, which has one analysis outlier. In addition to the previously described dilutions, an attempt was made to detect 4 μL of the second dilution experiment, which was 3.8 ppt of each component in the chamber, however, no signal can be collected at all. Therefore, at room temperature and 1 atm environment, this dynamic SPME sampling method coupled with GC/MS detection method can

provide reliable result for trace amount of terpene and terpenoid analysis. The concentration of terpene and terpenoid can reach as low as 7.57 ppt.

Table 5

The average peak area, standard deviation, percent relative standard deviation, and correlation coefficient of 3-carene, p-cymene, limonene, borneol, and isobornyl acetate at 757 ppt, 94.6 ppt, 75.7 ppt and 7.57 ppt.

Average peak area ±standard deviation (percent relative standard deviation)	3-carene[a] (Counts-min)	p-cymene[a] (Counts-min)	Limonene[a] (Counts-min)	Borneol[a] (Counts-min)	Isobornyl acetate[a] (Counts-min)
757 ppt	$(6.44\pm0.36)\times10^5$ 6%	$(8.65\pm0.58)\times10^5$ 7%	$(1.76\pm0.13)\times10^5$ 7%	$(1.89\pm0.18)\times10^5$ 9%	$(3.83\pm0.17)\times10^5$ 43%
94.6 ppt	$(1.02\pm0.06)\times10^5$ 6%	$(1.30\pm0.09)\times10^5$ 7%	$(2.53\pm0.19)\times10^4$ 7%	$(3.80\pm0.34)\times10^4$ 9%	$(6.71\pm1.5)\times10^4$ 22%
75.7 ppt	$(2.28\pm0.10)\times10^4$ 4%	$(3.09\pm0.21)\times10^4$ 7%	$(7.38\pm0.22)\times10^3$ 30%	$(9.16\pm0.78)\times10^3$ 9%	$(2.85\pm0.27)\times10^4$ 9%
7.57 ppt	$(3.13\pm0.28)\times10^3$ 9 %	$(4.18\pm0.30)\times10^3$ 7%	$(1.05\pm0.15)\times10^3$ 14%	$(1.21\pm0.09)\times10^3$ 7%	$(4.02\pm0.32)\times10^3$ 8%
R^2	0.9887	0.9938	0.9953	0.9871	0.9953

[a]Four SPME samples were collected for each compound from each chamber experiment.

3.7 Effect of Radical Scavenger on SPME Sampling Method

Secondary organic aerosol generation in laboratory chambers frequently use radical scavengers such as 2-butanol.[61] Radical scavengers react with hydroxyl radical and alkyl radicals (which are generated upon ozone/VOC reaction) and reduces the amount of secondary reactions of OH radical with VOCs that could occur. Therefore, the reaction of ozone and VOC can be isolated. 2-butanol was chosen as the radical scavenger in this study, since it doesn't contain any unsaturated carbon-carbon double bond, and it isn't sampled by the SPME fiber. The hypothesis is that the addition of 2-butanol does not have an effect on the SPME sampling method. The

average peak area of terpene mixture both with and without 2-butanol in chamber air are shown in Table 6. An F-test and a two-sample t-test were performed for all the terpenes/ terpenoids. All the results of F_{test} were smaller than $F_{critial}$, except borneol, which means only the standard deviations of borneol with/ without radical scavenge were significant different.. All the results of t-test were smaller than $t_{critical}$. For all of the five terpene compounds, vaporizing 250 μL liquid 2-butanol, which was 12.1 ppm in the smog chamber, did not make significant change in the peak area. Therefore, verified that adding 2-butanol did not have effect on the SPME sampling method.

Table 6

The average peak area, standard deviation, percent relative standard deviation, intercept, F test and t test value of 3-carene, p-cymene, limonene, borneol, and isobornyl acetate with and without 2-butanol.

Average peak area ±standard deviation (percent relative standard deviation)	3-carene	p-cymene	limonene	borneol	isobornyl acetate
without 2-butanol Counts-min	$(2.44\pm0.28)\times10^5$ 11%	$(2.96\pm0.44)\times10^5$ 15%	$(6.13\pm0.93)\times10^4$ 15%	$(7.40\pm1.2)\times10^4$ 17%	$(1.22\pm0.42)\times10^5$ 34%
with 2-butanol Counts-min	$(2.55\pm0.18)\times10^5$ 7.2%	$(3.11\pm0.26)\times10^5$ 8.2%	$(6.46\pm0.53)\times10^4$ 8.3%	$(6.94\pm0.49)\times10^4$ 7.0%	$(1.53\pm0.64)\times10^5$ 42%
F_{test}[a]	2.27	3.00	3.06	6.50	2.36
t test[b]	0.720	0.658	0.693	0.764	0.895

[a] $F_{critial}= 5.05$

[b] $t_{critial}= 2.306$

3.8 Terpenes/terpenoids Mixture Standard Curve

In order to verify that the dynamic SPME sampling method is a quantitative method, five concentrations of terpenes/terpenoids mixtures were examined under the same experimental

condition. The tests were performed on the same day, consecutively, without changing the sampling flow rate, sampling follow rate. The mixture included 3-carene, p-cymene, limonene, borneol, and isobornyl acetate. 8.00 μL, 8.00 μL, 24.0 μL, 40.0 μL, and 40.0 μL mixtures were vaporized into the same chamber in sequence. Because the volume of sample removed from the chamber for each sample (0.01 m^3) is negligible in comparison to the total chamber volume (5.5 m^3), on term of concentration, the concentration of terpenes/terpenoids mixture inside the chamber were 1.00×10^2 ppb, 2.00×10^2 ppb, 5.00×10^2 ppb, 1.00×10^3 ppb, and 1.50×10^3 ppb respectively, after each injection. Three replicate SPME samples were collected at each concentration. The amount of 3-carene, p-cymene, limonene, and borneol that extracted by this dynamic SPME sampling method were shown in Fig. 4, with R^2 values showing at Table 7. The GC/MS peak area response of these four compounds increased as the concentration increased in a linear relationship. The R^2 values were ranging between 0.98 and 0.99, which were deemed acceptable for use in quantification. The isobornyl acetate, on the other hand, did not demonstrate good linearity in this concentration range and poorer reproducibility as its concentration increased. This phenomenon may be related to the higher molecular weight and the polarity of the acetate group of isobornyl acetate. First, the equilibrium distribution of isobornyl acetate between PDMS/CAR fiber coating and sample matrix was more difficult to reach, with larger molecular weight. Also, since PDMS/CAR fiber is bipolar phase coating, and the polarity of the acetate group in isobornyl acetate is relatively strong, the distribution of isobornyl acetate between PDMS/CAR fiber and sample matrix was unstable. Since p-cymene has the smallest molar mass, it is relatively easy for it to transport to the SPME fiber when comparing with borneol and isobornyl acetate, which have larger molar mass. Therefore, the slope of p-cymene is the highest.

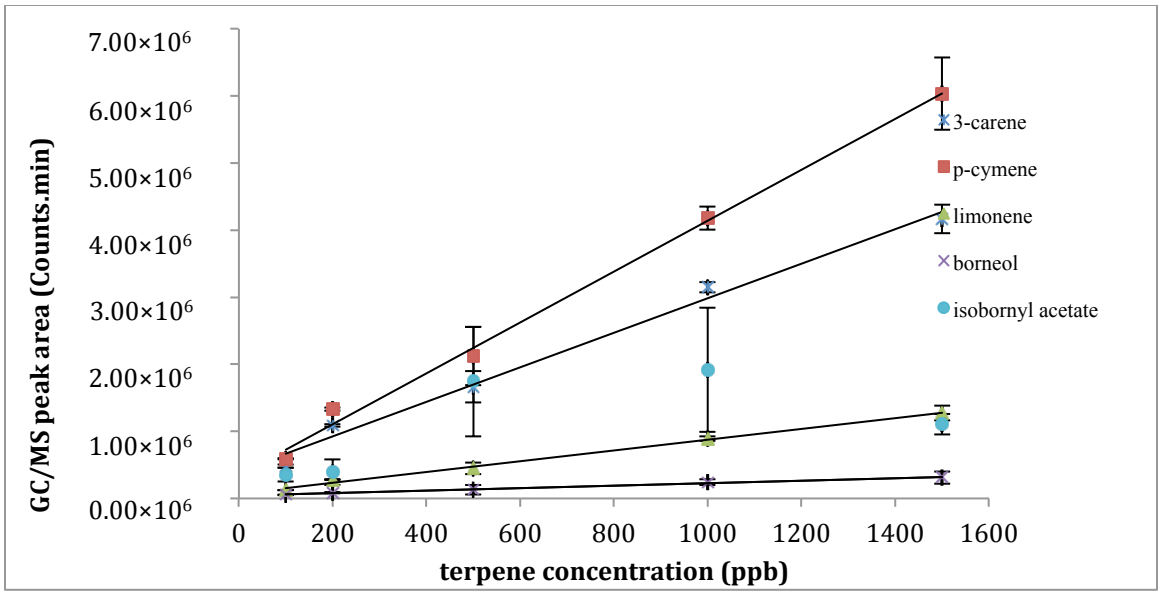

Figure 4. GC/MS peak area response of terpenes/terpenoids mixture at 100 ppb, 200 ppb, 500 ppb, 1000 ppb, and 1500 ppb under the same experimental condition using dynamic SPME sampling method coupled with GC/MS analysis method.

Table 7

The linear equations and R^2 values for p-cymene, 3-carene, borneol, and limonene in terpene/terpenoids mixture standard curve experiments

	Slope	Intercept	R^2
p-cymene	3794.3	347200	0.9956
3-carene	2754.7	410320	0.9890
borneol	183.88	43147	0.9934
limonene	802.71	73233	0.9954

3.9 Sampling Time Effects on SPME Sampling Method

The goal of SPME sampling is to reach the distribution equilibrium between the analyte absorbed on the SPME fiber and the analyte in the matrix. One important factor in reaching the equilibrium distribution is the equilibrium time, which is defined as the time required for the amount of extracted analyte to remain constant within experimental error. The equation $n=\frac{K_{fs}V_fV_sC_0}{K_{fs}V_f+V_s}$ [62] is used to describe the equilibrium condition. N is the amount of analyte extracted by the SPME fiber coating at equililibrium. K_{fs} is the distribution constant between fiber coating and sample matrix, V_f and V_s are the fiber coating volume and sampling volume, respectively. C_0 is the initial concentration of the given analyte in the sample matrix. As indicated by the equation above, n is independent from extraction time. Pawliszyn pointed out that the GC/MS response of the analyte increases rapidly at beginning of sampling, and followed by a slow increase related to the mass transfer of sample from the sample matrix to the SPME fiber.[63] The SPME sampling time is typically selected so that the equilibration time is reached. However, when equilibration times are too long for the analysis, a shorter sampling time can also be applied for quantitation, and the amount of analyte extracted by the SPME fiber coating is related to the sampling time. Therefore, in this study, the amount of analytes extracted by the SPME fiber coating has a linear relationship with the sampling time. Under this condition, in order to obtain reproducible data, constant convection to the fiber and careful timing for the extraction are critical.

In this work, the effect of sampling time was measured under the constant convection condition with careful extraction timing. Table. 9 shows the GC/MS peak area results for different sampling times for 3-carene, p-cymene, limonene, borneol, and isobornyl acetate. For

this experiment, the monoterpene mixture concentration, flow rate, relative humidity, temperature, and ozone concentration were held constant and carefully monitored. The sampling flow rate was controlled by the flow meter set to 5 L/min. The concentration of ozone was 3.14 ppb with 1 ppb standard deviation, and the temperature of the chamber was 22.8 °C with 0.4 °C standard deviation. The relative humidity was monitored during the experiment, and it was 1.10% with 0.10% standard deviation. As indicated by the table 9, the GC/MS response increased when sampling time increased. The relative standard deviations of the GC/MS peak areas of 3-carene, p-cymene, and limonene were ≤14% when the sampling time was between 2 and 15 minutes. The relative standard deviations of borneol were lower than 15% when sampling time are 5 minutes and 10 minutes, but the relative standard deviations increased to ≥21% for shorter sampling times and for longer sampling times. The relative standard deviations of isobornyl acetate were all larger than ≥25%, although the relative standard deviations were tended to be smaller for longer sampling times. Vereen et al. suggested that that less volatile terpenoids need longer sampling times (up to 3 hours) to reach the constant response when they used headspace SPME sampling method.[64] Borneol and isobornyl acetate are less volatile than 3-carene, p-cymene, and limonene, and the less volatile terpenoids have lower mass transfer rate compared with more volatile terpenes, which would affect the analyte mass transfer from sample matrix to SPME fiber.[59] Moreover, this will affect the reproducibility of this dynamic SPME sampling method. This maybe due to the chemical property of acetate and hydroxyl group on the structure, as the PDMS/CAR fiber is more suitable for non-polar compounds.

Table 8

Average peak area±standard deviation, and percent relative standard deviation of monoterpenes and terpenoids mixtures at different sampling times.

Average peak area ±standard deviation (percent relative standard deviation) (Counts-min)	2 min	5 min	10 min	30 min
3-carene	$(3.21\pm0.24)\times10^5$ (7.4%)	$(7.8\pm0.63)\times10^5$ 8.1%	$(13.6\pm0.32)\times10^5$ 2.3%	$(28.4\pm0.89)\times10^5$ 3.1%
p-cymene	$(3.85\pm0.53)\times10^5$ 14%	$(1.00\pm0.14)\times10^6$ 14%	$(1.94\pm0.10)\times10^6$ 5.3%	$(4.52\pm0.41)\times10^6$ 9.1%
limonene	$(7.94\pm1.1)\times10^4$ 14%	$(2.10\pm0.30)\times10^5$ 14%	$(4.07\pm0.22)\times10^5$ 5.5%	$(9.34\pm0.77)\times10^5$ 8.2%
borneol	$(8.19\pm1.7)\times10^4$ 21%	$(1.65\pm0.24)\times10^5$ 15%	$(3.19\pm0.19)\times10^5$ 6.1%	$(4.40\pm0.97)\times10^5$ 22%
isobornyl acetate	$(1.69\pm0.95)\times10^5$ 56%	$(5.47\pm2.6)\times10^5$ 48%	$(6.16\pm1.5)\times10^5$ 25%	$(1.98\pm0.61)\times10^6$ 30%

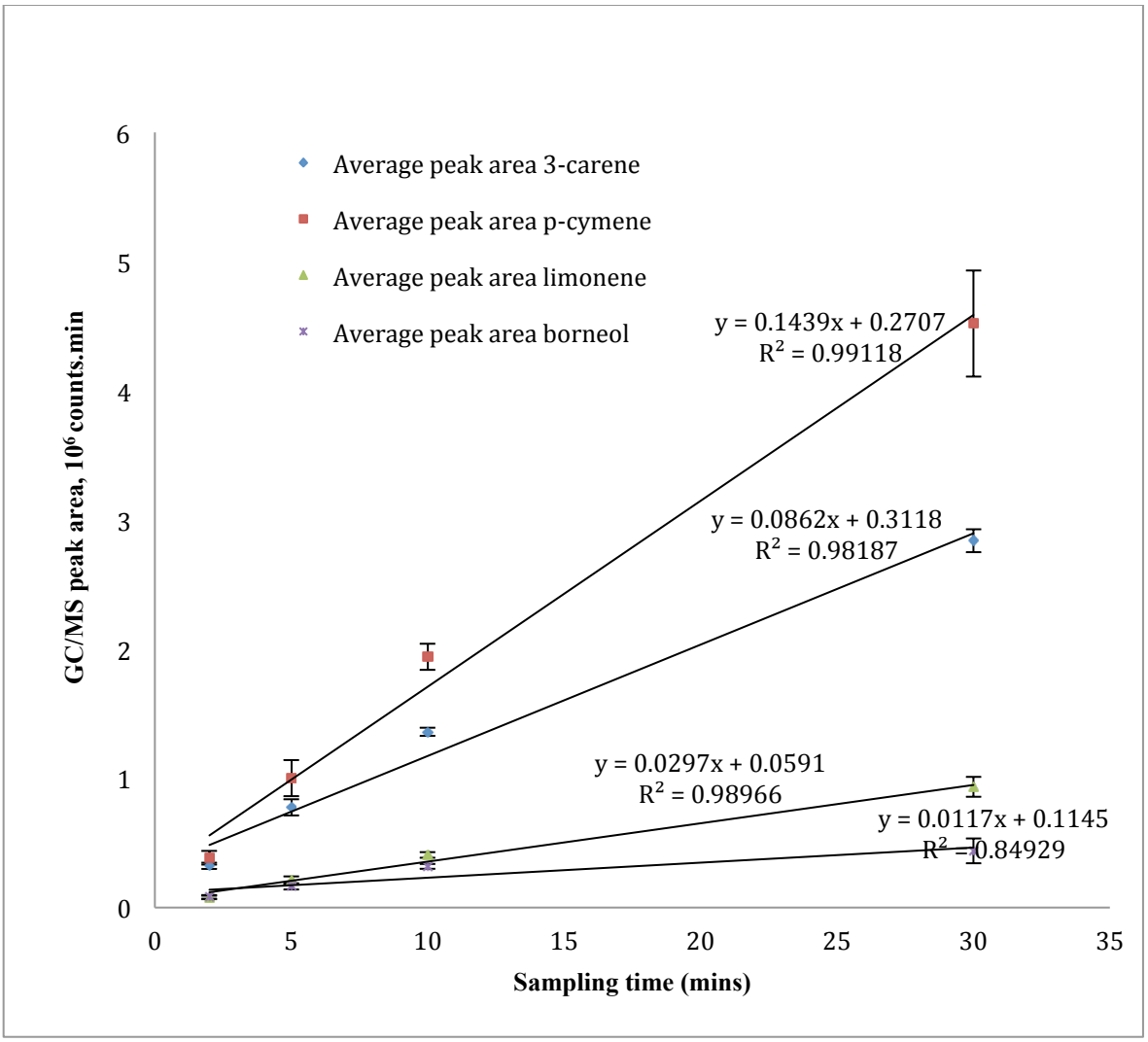

Figure 5. Average peak area, standard deviation and relative standard deviation of 3-carene, p-cymene, limonene, borneol at 2 minutes, 5 minutes, 10 minutes and 30 minutes. 4 replicates were collected at each sampling time. Error bars represent the standard deviation of the replicates.

3.10 Sampling Flow Rate Effects on SPME Sampling Method

As the equation $n=\frac{K_{fs}V_fV_sC_0}{K_{fs}V_f+V_s}$ [62] showing, the amount of analyte extracted by the SPME fiber coating is not related to the follow rate. Therefore, this study was designed to verify that the

variance of sampling follow rate will not have any impact on the dynamic SPME sampling method.

Figure 6 shows are the GC/MS response of monoterpene mixtures at different sampling flow rate, from 2 L/min, 5 L/min, 10 L/min to 20 L/min. Four SPME samples were collected at each sampling flow rate in order to verify the reproducibility of this sampling method. The F test and t-test had been performed between those two values with bigger difference All the F test results were smaller than $F_{critical,}$ except borneol, which means only the standard deviations of borneol at different sampling flow rates were significant different. The values of t test were all smaller than $t_{critical}$ for 7 degrees of freedom at 99.9% confidence. We observed that the higher flow rate does not significantly increase the GC/MS response, which suggests that the mass of monoterpenes that accumulated on the SPME fiber does not significantly change as flow rate is increased. Therefore, sampling flow rate does not have significant impact to this dynamic SPME sampling method for these analytes and between 2 and 20 L/min. All of the relative standard deviations are lower than 15%, except for isobornyl acetate. This poor reproducibility may due to the lower volatility of isobornyl acetate.

Table 9

The average peak area, standard deviation and relative standard deviation of monoterpene mixtures at different sampling flow rate.

Sampling flow rate	2 L/min	5 L/min	10 L/min	20 L/min
Average peak area 3-carene ±standard deviation (percent relative standard deviation) (Counts-min)	$(2.56\pm0.28)\times10^5$ 11%	$(3.03\pm0.22)\times10^5$ 7%	$(3.11\pm0.57)\times10^5$ 2%	$(3.21\pm0.24)\times10^5$ 4%
Average peak area p-cymene ±standard deviation (percent relative standard deviation) (Counts-min)	$(2.97\pm0.43)\times10^5$ 14%	$(3.53\pm0.33)\times10^5$ 9%	$(3.64\pm0.80)\times10^5$ 2%	$(3.19\pm0.14)\times10^5$ 5%
Average peak area limonene ±standard deviation (percent relative standard deviation) (Counts-min)	$(6.19\pm0.84)\times10^4$ 14%	$(7.38\pm0.68)\times10^4$ 9%	$(7.58\pm0.19)\times10^4$ 3%	$(6.75\pm0.33)\times10^4$ 5%
Average peak area borneol ±standard deviation (percent relative standard deviation) (Counts-min)	$(7.24\pm1.1)\times10^4$ 16%	$(8.56\pm1.3)\times10^4$ 15%	$(7.49\pm0.57)\times10^4$ 8%	$(7.57\pm0.97)\times10^4$ 13%
Average peak area isobornyl acetate ±standard deviation (percent relative standard deviation) (Counts-min)	$(1.64\pm0.83)\times10^5$ 51%	$(2.02\pm1.3)\times10^5$ 62%	$(1.76\pm1.2)\times10^5$ 66%	$(1.58\pm1.1)\times10^5$ 72%

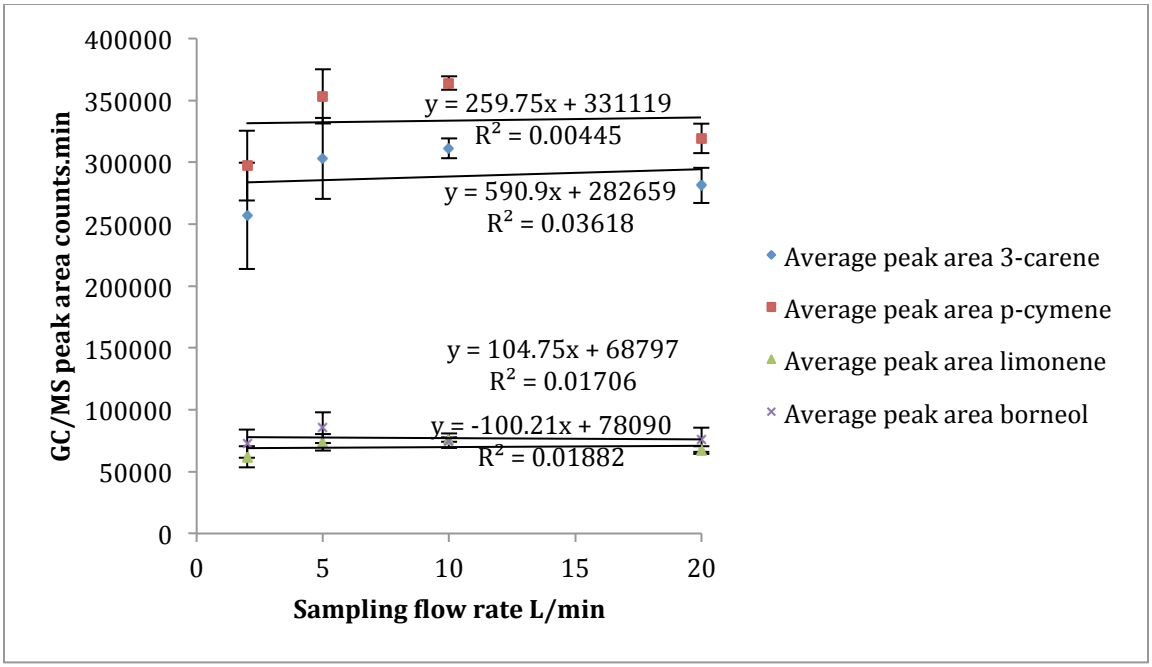

Figure 6. The average peak area, standard deviation and relative standard deviation of 3-carene, p-cymene, limonene and borneol at sampling flow rate of 2 L/min, 5 L/min, 10 L/min and 20 L/min. 4 replicates were collected at each sampling flow rate.

Table 10

The results of F test and t test of sampling flow rate experiments for 3-carene, p-cymene, limonene, borneol, and isobornyl acetate.

	3-carene	p-cymene	limonene	borneol	isobornyl acetate
F_{test}[a]	1.36	3.46	1.40	19.55	0.716
T test[b]	3.53	1.48	1.55	3.51	0.517

[a] $F_{critial}$= 9.28 at 95% confidence level

[b] $t_{critial}$= 2.447 at 95% confidence level

[b] $t_{critial}$= 4.029 at 99.5% confidence level

3.11 SPME Sampling under Various Ozone Concentrations

My previous studies showed that the dynamic SPME sampling method coupled with GC/MS detection method can be used for the gas-phase analysis of single and mixtures of terpenes/terpenoids. In an indoor environment, ozone is also present in the gas phase, which can rapidly react with certain terpenes/terpenoids to form PM. Nga et al. showed the minimum and maximum ozone concentration ranged from 2 ppb to 98 ppb in several buildings, including restaurants, hospitals, schools, and offices.[65] The concentration of ozone in indoor environment depended on several factors, such as the outdoor ozone concentration, the building materials, the air exchange rate, and the chemical reactions between ozone and other indoor chemicals.[66] Many smog chamber experiments use ozone as the oxidant for secondary organic aerosol generation. Thus, a series of experiments were conducted in order to verify the effect of different ozone concentrations on the sampling method. Four target ozone concentrations levels were selected to cover the range of typical ozone concentrations used in smog chamber experiments: ≤100 ppb, ≈ 200 ppb, ≈ 600 ppb, and ≥ 1000 ppb. The ozone generator was used to generate different concentrations of ozone in the chamber, with a continuous ozone analyzer to monitor the ozone concentration. Due to the uneven ozone distribution in the smog chamber at the beginning of sampling period, the ozone concentrations measured by ozone analyzer didn't reflect the final ozone concentration in the chamber. Therefore, the ozone concentration measurements taken at the begin 30 min were dropped. The average ozone concentrations shown in Table 11 represent the best estimate of the ozone concentration in the chamber as a function of the amount of time the ozone generator was applied.

Table 11

Average ozone concentration in chamber produced by ozone generator at level 0 for for 1.0 min, 2.0 min, 4.0 min, and 6.0 min.

Time	1.0 min	2.0 min	4.0 min	6.0 min
Average Ozone Concentration ±standard deviation (percent relative standard deviation) (ppb)	73±5 7%	258±13 5%	619±24 4%	1084±55 5%

To determine the effect of ozone on the SPME sampling method, 8 µL of the terpenes/terpenoids mixture, including 3-carene, p-cymene, limonene, borneol, and isobornyl acetate, was injected into the chamber first, followed by the addition of 250 µL of liquid 2-butanol. Four SPME samples, used as control samples, were collected by sampling the chamber prior to the addition of ozone. To generate the ozone, the ozone generator was turned on for 1 min., 2 min., 4 min., and 6 min. at level 0 for each experiment which produced a reproducible range of ozone concentrations from 70 ppb to 1100 ppb (Table 11). Five SPME samples were collected every half hour after ozone had been injected into the chamber.

The reaction rate of borneol, p-cymene, and isobornyl acetate with ozone is negligible.[59] Student t-tests were performed to verify there is no significant difference at 95% confidence level between in the average peak areas of borneol, p-cymene, and isobornyl acetate taken before and after adding ozone. The SPME sampling method was not affected by high ozone concentration for these compounds.

Table 12

The results of F-test and t-test of p-cymene, borneol, and isobornyl acetate at various ozone concentrations.

Ozone Concentration ppb		73±5	258±13	619±24	1084±55
P-cymene	F_{test}[a]	9.33	1.53	5.60	2.53
	t test[b]	0.237	0.530	2.82	1.40
Borneol	F_{test}[a]	2.73	2.19	1.22	4.06
	t test[b]	0.360	1.19	0.293	1.09
Isobornyl Acetate	F_{test}[a]	0.295	0.933	7.12	0.998
	t test[b]	0.119	0.870	1.40	0.313

[a]$F_{critial}$= 5.41

[b]$t_{critial}$= 2.262

Limonene can't be detected in any of the samples when the ozone concentration levels were 600 ppb and 1100 ppb. This is consistent with the kinetics of limonene/ozone reaction. At 298 K, the half-life of limonene is 224 s in the presence of 600 ppb ozone and 123 s in the presence of 1100 ppb ozone assuming pseudo first order kinetics. No limonene was detected because the first SPME sample was collected at 1800 s after the VOC mixture was added to the chamber. When the ozone concentration was lower (70 ppb), limonene can be detected as long as the sample is collected within 2 hours. The pseudo first order rate constant k of limonene that calculated by the experiment result, when ozone concentration was 73±5 ppb, was 6×10^{-4} s^{-1}. The pseudo first order rate constant k of limonene that calculated from the literature second-order rate constant was 3.9×10^{-4} s^{-1}.[59] However, when ozone concentration was at 250 ppb level, only 2% of limonene can be detected after 1 hour. When ozone concentration was 258±13 ppb, the

experimental first order rate constant k of limonene, which was calculated by secondary order rate constant of limonene × concentration of ozone, was 1.1×10^{-4} s^{-1} , and the literature rate constant was 1.3×10^{-4} s^{-1} . The agreement between these two values is within 20%, which is a good agreement. In contrast, 3-carene can be detected even after 2 hours when ozone concentration level was 250 ppb level. 3-carene has smaller ozone rate constant, 3.7×10^{-17} cm^3 $molec^{-1}$ s^{-1} at 298 K and 1 atm in comparison to limonene, 21×10^{-17} cm^3 $molec^{-1}$ s^{-1}.[59] The first rate constants k of 3-carene at various ozone concentration ,showing in Table 15, that were calculated from experiment result were different from the value that calculated from literature result. One of the possible reasons could be the inconsistent ozone concentration inside the chamber or that pseudo first order kinetics are not achieved. However, we detect no systematic effect of ozone on SPME sampling for non ozone-reactive VOCs. For ozone-reactive VOCs, ozone reduces the concentration of VOCs due to direct reaction rather than sampling artifact. However, we cannot rule out a sampling artifact specific to ozone-reactive monoterpenes at this time.

Table 13

Peak area of limonene at 73±5 ppb ozone concentration.

Min.	Second	Peak Area
0	0	1.16×10^{5}
33	1980	1.30×10^{4}
58	3480	1.38×10^{4}
83	4980	7.22×10^{3}
108	6480	1.35×10^{3}
133	7980	nd[a]
167	10020	nd[a]

[a]nd = none detected

Table 14

Peak area and % peak area of limonene at 258±13 ppb ozone concentration.

Min.	Second	Peak Area	% Peak Area
0	0	2.24×10^{5}	100%
28	1680	1.28×10^{4}	6%
56	3360	5.53×10^{3}	2%
87	5220	nd[a]	nd[a]
117	7020	nd[a]	nd[a]
145	8700	nd[a]	nd[a]
177	10620	nd[a]	nd[a]

[a]nd = none detected

Table 15

The experimental and literature first rate constant k of 3-carene at various ozone concentration.

Ozone Concentration ppb	Experimental first rate constant k s^{-1}	Literature first rate constant k s^{-1}
73±5	1.0×10^{-4}	0.67×10^{-4}
258±13	3.3×10^{-4}	2.4×10^{-4}
619±24	3.4×10^{-2}	0.55×10^{-3}
1084±55	4.4×10^{-2}	0.98×10^{-3}

Table 16

The experimental and literature first rate constant k of limonene at various ozone concentration.

Ozone Concentration ppb	Experimental first rate constant k s^{-1}	Literature first rate constant k s^{-1}
73±5	6.0×10^{-4}	3.8×10^{-4}
258±13	1.1×10^{-4}	1.3×10^{-4}

CHAPTER 4

CONCLUSION AND FURTHER WORK

The wide use of some terpenes and terpenoid-containing household products results in plentiful indoor concentrations of terpenes and terpenoids.The reactions of ozone and terpenes/terpenoids dominate the indoor air chemistry.[12] However, there is neither enough knowledge to identify the compounds formed in ozone terpenes/terpenoids reactions nor adequate toxicology information regarding the relationship between indoor chemistry and human health. It is critical to develop a high efficient sampling method coupled with detection method for terpenes/ terpenoids in indoor environment, in order to provide fundamental information to further research and protections.

In this thesis, we have developed a dynamic SPME sampling method coupled with GC/MS detection method and demonstrated that the dynamic SPME sampling method is a fast, precise, and organic solvent-free method for qualitative study of single terpenes/terpenoids and complex terpenes/terpenoids mixtures in the gas phase. A series of reproducibility experiments were conducted for limonene, 3-carene, p-cymene, borneol, eucalyptol, α-phellandrene, and isobornyl acetate. The range of RSD values was from 7.0% to 17.9% of each experiment. These RSD values demonstrated that the SPME/GCMS method was a suitable method for certain terpenes/terpenoids detection in the gas phase. The reproducibility of a mixture of terpenes and terpenoids made from previous mentioned compounds was also measured. The RSD values were lower than 10% expect for isobornyl acetate. The detection limit of this method for terpenes/terpenoids can reach as low as 1 ppb with acceptable RSD values, lower than 15%. We also performed experimental optimization studies of the dynamic SPME sampling method. These

studies evaluate the effects of sampling time, sampling flow rate, radical scavenger, and ozone concentration on the reproducibility of the SPME/GCMS method. These studies have suggested that sampling flow rate, ranging from 2 to 20 L/min and the presence or absence of radical scavenger did not have significant effect on the sampling method and the reproducibility of the method and GCMS peak area response of terpenes/terpenoids remained the same. However, the sampling time did have significant effect on the sampling method. The GCMS peak area response of terpenes/ terpenoids changed by an order of magnitude when the sampling time changed from 2 min. to 30 min. This sampling method can be performed under variant high ozone concentrations conditions, from 70 ppb to 1100 ppb. The reactive VOCs can be collected by the dynamic SPME sampling method before they completely reacted with ozone. The non-reactive VOCs also can be collected by the dynamic SPME sampling method no matter what ozone concentration was. The student t tests verified that these no significant difference between the samples collected with and without ozone. Therefore, the ozone concentration can be as high as 1100 ppb without any impact on the dynamic SPME sampling method.

Further work can be performed to use this SPME sampling method for quantitative analysis of various household products in real indoor environment. The poor precision problems for α-pinene and β-pinene analysis need to be addressed.

REFERENCES

(1) United States Environmental Protection Agency. Particulate Matter Basic Information. http://www.epa.gov/airquality/particlepollution/basic.html

(2) Singer, B. C.; Coleman, B. K.; Destaillats, H.; Hodgson, A. T.; Lunden, M. M.; Weschler, C. J.; Nazaroff, W. W. Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. *Atmos. Environ.* **2006**, *40*, 6696–6710.

(3) Yassaa, N.; Williams, J. Enantiomeric monoterpene emissions from natural and damaged Scots pine in a boreal coniferous forest measured using solid-phase microextraction and gas chromatography/mass spectrometry. *J. Chromatogr A*, **2007**, *1141*, 138–144.

(4) Yu, J.; Cocker III, D. R.; Griffin, R. J.; Flagan, R. C.; Seinfeld, J. H. Gas-Phase Ozone Oxidation of Monoterpenes: Gaseous and Particulate Products. *J. Atmos. Chem.* **1999**, *34*, 207–258.

(5) Pachauri, R. K.; Reisinger, A. IPCC Fourth Assessment Report. Climate Change 2007: Synthesis Report.

(6) Papiez, M. R.; Potosnak, M. J.; Goliff, W. S.; Alex B. Guenther, A. B.; Matsunaga, S. N.; Stockwell, W. R. The impacts of reactive terpene emissions from plants on air quality in Las Vegas, Nevada. *Atmos. Environ.* ***2009****, 43*, 4109–4123.

(7) Su, H. J.; Chao, C. J.; Chang, H. Y.; Wu, P. C. The Effects of Evaporating Essential Oils on Indoor Air Quality. *Atmos. Environ*. **2007**, *41*, 1230–1236.

(8) Ostro, B. D.; Hurley, S.; Lipsett, M. J. Air pollution and daily mortality in the Coachella Valley, California: a study of PM10 dominated by coarse particles. *Environ. Res.* **1999,**

81, 231-238.

(9) United States Environmental Protection Agency. National Ambient Air Quality Standards for Particulate Matter; Final Rule. 2013 http://www.gpo.gov/fdsys/pkg/FR-2013-01-15/pdf/2012-30946.pdf

(10) Hakola, H.; Shorees, B.; Arey, J.; Atkinson, R. Product formation from the gas-phase reactions of hydroxyl radicals and ozone with beta-phellandrene. *Environ. Sci. Technol.* **1993,** *27*, 278–283

(11) Schäfer, B.; Hennig, P.; Engewald, W. Analysis of monoterpenes from conifer needles using solid phase microextraction. *J. High Resolut. Chromatogr.* **2005,** *18*, 587-592.

(12) Kephalopoulos, S.; Kotzias, D.; Koistine, K. Impact of Ozone-initiated Terpene Chemistry on Indoor Air Quality and Human Health. EUR 23052 EN. European Collaborative Action "Urban Air, Indoor Environment and Human Exposure". **2007.**

(13) Tholl, D.; Christine M. Kish, C. M.; Orlova, I.; Sherman, D.; Jonathan Gershenzon, J.; Pichersky, E.; Dudarev, N. Formation of Monoterpenes in *Antirrhinum majus* and *Clarkia breweri* Flowers Involves Heterodimeric Geranyl Diphosphate Synthases. *The Plant Cell,* **2004,** *16,* 977–992.

(14) Singer, B.C.; Coleman, B.K.; Destaillats, H.; Hodgson, A.T.; Lunden, M.M.; Weschler, C.J.; Nazaroff, W.W. Indoor Secondary Pollutants from Cleaning Product and Air Freshener Use in the Presence of Ozone. *Atmos. Environ*. **2006**, *40*, 6696-6710.

(15) Nazaroff, W.W.; Weschler, C.J. Cleaning Products and Air Fresheners: Exposure to Primary and Secondary Air Pollutants. *Atmos. Environ.* **2004,** *38*, 2841–2865.

(16) Sack, T. M.; Steele, D. H.; Hammerstrom, K.; Remmers, J. A Survey of Household Products for Volatile Organic Compounds. *Atmo. Environ. A-Gen.* **1992,** *26,* 1063-1070.

(17) Kwon, K., Jo, W., Lim, H.; Jeong, W. Characterization of Emissions Composition for Selected Household Products Available in Korea. *J. Hazard. Mater.* **2007,** *148,* 192-198

(18) United States Environmental protection Agency. National Trends in Ozone Levels. http://www.epa.gov/airtrends/ozone.html

(19) Weschler, C. J. Ozone in Indoor Environments: Concentration and Chemistry. *Indoor Air,* **2000,** *10,* 269–288.

(20) Weschler, C.J.; Shields, H.C. Indoor Ozone/terpene Reactions as a Source of Indoor Particles. *Atmos. Environ*. **1999**, *33*, 2301-2312

(21) Weschler, C.J.; Shields, H.C. Potential Reactions Among Indoor Air Pollutants. *Atmos. Environ*. **1997**, *31*, 3487–3495

(22) Berndt, T.; Boge, O.; Stratmann, F. Gas-phase Ozonolysis of α-pinene: Gaseous Products and Particle Formation. . *Atmos. Environ*. **2003**, *37*, 3933–3945

(23) Calogirou, A.; Larsen, B.R.; Kotzias, D. Gas-phase Terpene Oxidation Products: A Review. *Atmos. Environ*. **1999**, *33*, 1423–1439

(24) Amin, H. S. Speciation Studies for Biogenic Volatile Organic Compounds and Secondary Organic Aerosol Generated by Ozonolysis of Volatile Organic Compound Mixtures. Ph. D. Dissertation, Southern Illinois University, Carbondale, IL, April 2012.

(25) Sundell, J. On the history of indoor air quality and health. *Indoor Air,* **2004,** *14,* 51–58.

(26) Phalen, R. F. The Particulate Air Pollution Controversy. *Nonlinearity Biol. Toxicol. Med.,* **2004,** *2,* 259–292.

(27) Anderson, J.O.; Thundiyil J.G.; Stolbach, A. Clearing the Air: A Review of the Effects of Particulate Matter Air Pollution on Human Health. *J. Med. Toxicol.* **2012**, *8*,166-175.

(28) Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, ed. D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor and H. L. Miller, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007.

(29) Nadadur, S. S.; Miller, A.; Hopke, P. K.; Gordon, T.; Sverre Vedal, S.; Vandenberg, J. J.; Daniel L. Costak, D. L. The Complexities of Air Pollution Regulation: the Need for an Integrated Research and Regulatory Perspective. *Toxicol. Scil.* **2007,** *100,* 318–327

(30) Dockery, D. W.; Pope, CA. 3rh.; Xu, X.; Spengler, J. D.; Ware, J. H.; Fay, M. E.; Ferris, BG. Jr.; Speizer, F. E. An Association between Air Pollution and Mortality in Six U.S. Cities. *N. Engl. J. Med.* **1993**, *329*, 1753-1759

(31) Anderson, J.O.; Thundiyil J.G.; Stolbach, A. Clearing the Air: A Review of the Effects of Particulate Matter Air Pollution on Human Health *J. Med. Toxicol.* **2012**, *8*, 166-175

(32) Pope, CA. 3rh.; Thun, M. J.; Namboodiri, M. M.; Dockery, D. W.; Evans, J. S.; Evans, J. S.; Speizer, F. E.; Heath, CW. Jr. Particulate Air Pollution as a Predictor of Mortality in a Prospective Study of U.S. Adults. *Am. J. Respir. Crit. Care Med.* **1995**, *151*, 669–674

(33) Omori, T.; Fujimoto. G.; Yoshimura, I.; Nitta, H.; Ono, M.; Effects of Particulate Matter on Daily Mortality in 13 Japanese Cities. *J. Epidemiol.* **2003**, *13*, 314–322

(34) Barnett, A. G.; Williams, G. M.; Schwartz, J.; Best T. L.; Neller, A. H.; Petroeschevsky, A. L.; Simpson, R. W. The Effects of Air Pollution on Hospitalizations for Cardiovascular Disease in Elderly People in Australian and New Zealand Cities. *Environ. Health. Perspect*. **2006**,*114*, 1018–1023

(35) Pepelko, W. E.; Feasibility of dose adjustment based on differences in long-term

clearance rates of inhaled particulate matter in humans and laboratory animals. *Regual. Toxical. Pharm.* **1987,** *7,* 236-252

(36) Isaksen, I. S. A.; Granier, C.; Myhre, G.; Berntsen, T. K.; Dals.ren, S. B.; Gauss, M.; Klimont, Z.; Benestad, R.; Bousquet, P.; Collins, W.; Cox, T.; Eyring, V.; Fowler, D.; Fuzzi, S.; Jöckel, P.; Laj, P.; Lohmann, U.; Maione, M.; Monks, P.; Prevot, A. S. H.; Raes, F.; Richter, A.; Rognerud, B.; Schulz, M.; Shindell, D.; Stevenson, D. S.; Storelvmo, T.; Wang, W.C.; van Weele, M.; Wild, M.; Wuebbles, D. Atmospheric Composition Change: Climate–Chemistry Interactions. *Atmos. Environ.* **2009**, *43*, 5138–5192.

(37) Meier, J.; Tegen, I.; Heinold, B.; Wolke, R. Direct and semi-direct radiative effects of absorbing aerosols in Europe: Results from a regional model. *Geophys. Res. Lett.* **2012,** *39,* L09802.

(38) Lohmann, U.; Feichter, J. Global Indirect Aerosol Effects: A Review. *Atmos. Chem. Phys.* **2005**, *5*, 715–737

(39) Koch, D.; Del Genio, A. D. Black Carbon Semi-direct Effects on Cloud Cover: Review and Synthesis. *Atmos. Chem. Phys.* **2010,** *10*, 7685-7696

(40) Hallquist, M.; Wenger, J. C.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N. M.; George, C.; Goldstein, A. H.; Hamilton, J. F.; Herrmann, H.; Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M. E.; Jimenez, J. L.; Kiendler-Scharr, A.; W. Maenhaut, W.; McFiggans, G.; Mentel, Th. F.; Monod, A.; Prev´ otˆ, A. S. H.; Seinfeld, J. H.; Surratt, J. D.; Szmigielski, R.; Wildt, J. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.,* **2009,** *9,* 5155–5236.

(41) Donahue, N. M.; Huff Hartz, K. E.; Chuong, B.; Presto., A. A.; Stanier, C. O.; Rosenørn, T.; Robinson, A. L.; N. Pandis, S. N. Critical factors determining the variation in SOA yields from terpene ozonolysis: A combined experimental and computational study. *Faraday Discuss*. **2005**,*130,* 295-309.

(42) S. Youssefi, M. S. Waring. Predicting secondary organic aerosol formation from terpenoid ozonolysis with varying yields in indoor environments. *Indoor Air.* **2012**, 415–426.

(43) Emily A. Weitkamp , Amy M. Sage , Jeffrey R. Pierce , Neil M. Donahue , and Allen L. Robinson. Organic Aerosol Formation from Photochemical Oxidation of Diesel Exhaust in a Smog Chamber. *Environ. Sci. Technol.* **2007**, 6969–6975.

(44) Ramírez, N.; Cuadras, A.; Rovira, E.; Borrull, F.; Marcé, R. M. Comparative study of solvent extraction and thermal desorption methods for determining a wide range oof volatile organic compounds in ambient air. *Talanta*. **2010,** *82,* 719–727.

(45) Miracolo1, M. A.; C. J. Hennigan, c. j.; Ranjan, M.; Nguyen, N. T.; Gordon, T. D.; E. M. Lipsky, E. M.; Presto, A. A.; Donahue, N. M.; Robinson, A. L. Secondary aerosol formation from photochemical aging of aircraft exhaust in a smog chamber. *Atmos. Chem. Phys.* **2011,** *11,* 4135–4147.

(46) Arthur, C. L.; Pawliszyn, J. Solid Phase Microextraction with Thermal Desorption Using Fused Silica Optical Fibers. *Anal. Chem.* **1990,** *62*, 2145–2148.

(47) Ouyang, G.; Zhao, W.; Alaee, M.; Pawliszyn, J. Time-weighted average water sampling with a diffusion-based solid-phase microextraction device. *J. Chromatogr. A.* **2007,** *1138*, 42-46.

(48) Chen, J.; Pawliszyn, J. Solid Phase Microextraction Coupled to High-Performance Liquid

Chromatography. *Anal. Chem.* **1995,** 67, 2530–2533.

(49) Zhou, F.; Li, X.; Zeng, Z. Determination of Phenolic Compounds in Wastewater Samples Using a Novel Fiber by Solid-phase Microextraction Coupled to Gas Chromatography. *Anal. Chim. Acta.* **2005**, *538*, 63–70

(50) Navalon, A.; Prieto, A.; Araujo, L.; Vilchez, J. L. Determination of Pyrimethanil and Kresoxim-methyl in Soils by Headspace Solid-phase Microextraction and Gas Chromatography-mass Spectrometry. *Anal. Bioanal. Chem.* **2004**, *379*, 1100–1105

(51) ISI Web of Knowledge.

http://www.epa.gov/airquality/particlepollution/basic.html

(51) Yassaa, N.; Williams, J. Enantiomeric monoterpene emissions from natural and damaged Scots pine in a boreal coniferous forest measured using solid-phase microextraction and gas chromatography/mass spectrometry. *J. Chromatogr. A*, **2007**, *1141,* 138–144

(52) Pawliszyn, J. Solid phase microextraction - theory and practice. Wiley-VCH, New York, **1997,** 97-101.

(53) Pawliszyn, J. Solid phase microextraction - theory and practice. Wiley-VCH, New York, **1997,** 123-125.

(54) Hatfield, M. L Particulate Matter yields and secondary organic aerosol production from atmospheric biogenic precursor mixtures. Master thesis, Southern Illinois University Carbondale, Carbondale, U.S.A. 2010.

(55) Pawliszyn, J. *Solid Phase Microextraction: Theory and Practice.,* 1st edition. Wiley-VCH. 1997. Page 23.

(56) Spietelun, A.; Pilarczyk, M.; Kloskowski, A.; Namieśnik, J. Current trends in solid-phase microextraction (SPME) fibre coatings. *Chem. Soc. Rev.* **2010,** *39,* 4524-4537.

(57) Pawliszyn, J. *Solid Phase Microextration: Theory and Practice.* 1st edition. Wiley-VCH. 1997. Page 97-101.

(58) Wercinski, S. A. *Solid Phase Microextraction: a Practical Guide.* 1st edition. CRC Press. 1999. Chapter 3.

(59) Roger Atkinson, R.; Arey, J. Atmospheric Degradation of Volatile Organic Compounds. *Chem. Rev.* **2003,** *103,* 4605-4638.

(60) Augusto, F.; Koziel, J.; Pawliszyn, J. Design and Validation of Portable SPME Devices for Rapid Field Air Sampling and Diffusion-Based Calibration. *Anal. Chem.* **2001,** *73,* 481–486.

(61) Jonsson, Å. M.; Hallquist, M.; Ljungström, E. Influence of OH Scavenger on the Water Effect on Secondary Organic Aerosol Formation from Ozonolysis of Limonene, Δ3-Carene, and α-Pinene. *Environ. Sci. Technol.* **2008,** *42,* 5938–5944.

(62) Pawliszyn, J. Solid Phase Microextraction: Theory and Practice., 1st edition. Wiley-VCH. 1997. Page 23.

(63) Pawliszyn, J. Solid Phase Microextraction: Theory and Practice., 1st edition. Wiley-VCH. 1997. Page 17.

(64) Vereen, D. A.; McCall, J. P.; Butcher, D. J. Solid phase microextraction for the determination of volatile organics in the foliage of Fraser fir. *Microchem. J.* **2000,** *65,* 269-276

(65) Ng, L. C.; Musser, A.; Persily, A. K.; Emmerich, S. J. Indoor air quality analyses of

commercial reference buildings. *Build. Environ.* **2012,** *58,* 179–187.

(66) Weschler, C. J. Ozone in Indoor Environments: Concentration and Chemistry. *Indoor Air,* **2000,** *10,* 269–288.

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