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The Hong Kong Polytechnic University
Department of Civil and Structural Engineering

ENVIRONMENTAL CHAMBER STUDY ON THE FORMATION OF INDOOR SECONDARY ORGANIC AEROSOLS FROM HOUSEHOLD EMISSIONS

By

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CERTIFICATE OF ORIGINALITY

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ABSTRACT

Biogenic volatile organic compounds (BVOCs) are commonly used as solvents or odorants in household cleaning products and air fresheners that are utilized regularly for hygiene purposes in indoor environments. However, these BVOCs are unsaturated and very reactive, which can react rapidly with indoor oxidants such as ozone (O_3) to produce secondary organic aerosols (SOAs) and secondary gaseous pollutants. These generated secondary pollutants can impose adverse effects on human health. Furthermore, the formation of indoor secondary pollutants from indoor gas-phase reactions can be influenced by environmental parameters including air exchange rate (ACH), relative humidity (RH) and temperature (T), and the co-existence of other indoor gaseous pollutants such as ammonia (NH_3). Hence, in order to scientifically assess indoor air quality (IAQ) problems caused by secondary pollutants, it is important to characterize the BVOCs components in cleaning products and air fresheners popularly used in Hong Kong, and to investigate the effect such parameters have on the indoor secondary pollutants formation.

Solid-phase microextraction (SPME) coupling with gas chromatography/mass spectrometry (GC/MS) method was optimized for the determination of BVOCs in indoor environment. Parameters influencing the extraction processes, including sampling time, temperature and relative humidity were also investigated. Comparison studies were carried out on a set of floor cleaner extracts using the SPME method and traditional liquid injection method. Good agreement of the target BVOCs was obtained by the two methods.

The optimized SPME-GC/MS method was then applied for the determination of BVOCs compositions in three categories of cleaning products including floor cleaners (FC), kitchen cleaners (KC) and dishwashing detergent (DD), and air fresheners (AF). The analysis results showed that the chemical compositions and concentrations of individual BVOC varied broadly with household products in the view of their different functions and scents.

The effects of ACH, T, and RH on the formation of indoor SOAs through ozonolysis of BVOCs emitted from FC samples were investigated. Oxidation-generated secondary carbonyl compounds were also quantified. Acetone was the most abundant carbonyl compound. The formation mechanisms of formaldehyde and acetone were tentatively proposed in this study.

The effect of NH_3 on secondary pollutants formation from ozonolysis of BVOCs emitted from cleaning products including FC, KC and DD were investigated in a large environmental chamber. Our results demonstrated that the presence of NH_3 can significantly enhance SOAs formation regarding all the three categories of cleaning products. The percent yields (%) of secondary carbonyl compounds generated from ozonolysis of BVOCs emitted from the cleaning products were assesed in the presence and absence of NH_3.

Results obtained in this study will not only improve our understanding of the factors that influence the formation of ozone-derived SOAs but also assist home residents in improving IAQ through selecting appropriate cleaning products and air fresheners.

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2. **Huang, Y.**; Ho, S. S. H.; Ho, K. F.; Lee, S. C.; Gao, Y.; Cheng, Y.; Chan, C. S., Characterization of Biogenic Volatile Compounds (BVOCs) in Cleaning Reagents and Air Fresheners in Hong Kong. *Atmospheric Environment* 2011, 45, 6191-6196.
3. **Huang, Y.**; Ho, S. S. H.; Ho, K. F.; Lee, S. C.; Gao, Y.; Feng, N. S. Y., Optimization of Solid-phase Microextraction (SPME) to Determine Airborne Biogenic Volatile Organic Compounds (BVOCs): An Application for Measurement of Household Cleaning Product. *Aanalytical Methods* 2012**,** *4,* 277-283.
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Chapter 1 Introduction

1.1 Background

Indoor air quality (IAQ) has attracted more and more concerns, as a result of reports of symptoms or specific diseases that occur mainly in air-conditioned and mechanically ventilated buildings (Daisey et al., 2003). Indoor air pollutants can originate from a range of sources including the activities of building occupants and other biological sources, the combustion of substances for heating or fuel, and emissions from building materials (Jones, 1999; Lee et al., 2002a; Lee et al., 2002b). Infiltration from outside can also be another important source for some contaminants.

Concentrations of many volatile organic compounds (VOCs) are consistently higher indoors than outdoors, some of which may have short- and long-term adverse health effects (Guo et al., 2009). VOCs (including carbonyls) are found in adhesives, organic paints, houseplants, toiletries, air fresheners, and general household cleaning products (Guo et al., 2009). Hong Kong is one of the most densely populated cities in the world. More than 70% of the population live in a small apartment with an area averaging less than 70 m^2 (Li et al., 2006). Due to limited landscape, tall commercial and residential buildings are closely developed which block wind and lead to inefficient exhaust from indoor to outdoor environments. Any residential emission sources such as VOCs emissions from household cleaning products and air fresheners can highly affect IAQ. The impacts of indoor pollutants are amplified because (a) people spend a high proportion of their time indoors, (b) emissions that occur indoors are diluted into confined volumes and removed at slow ventilation rates, and (c) people tend to be in close proximity to indoor pollutant sources (Nazaroff, 2008).

A number of cleaning products and air fresheners routinely used indoors contain chemicals such as monoterpenes and other unsaturated VOCs (Nazaroff and Weschler, 2004). Owing to their natural origin, terpenes and terpene alcohols are always classified as biogenic volatile organic compounds (BVOCs) to differentiate them from those generated by anthropogenic sources (AVOCs). These BVOCs are reactive and are prone to be oxidized by indoor ozone, OH and nitrate radicals (Weschler, 2004). Ozone is ubiquitous in the indoor environment. It can penetrate into the indoor environment by infiltration and ventilation (Weschler, 2000b). Additionally, it can be directly emitted indoors from photocopiers, printers and air cleaning devices (Weschler, 2000b). Typical indoor ozone concentrations range from 1 to 100 $\mu g\ m^{-3}$.

Previous studies evidenced that secondary air pollutants including gaseous pollutants and particulate matters (PM) can be formed by interactions between terpenes and ozone in the indoor environment. For example, a significant degree of secondary particle growth was observed immediately upon mixing of household products and ozone in the chamber study conducted by Destailats et al. (2006). Toftum et al. (2008) examined the formation and growth of SOAs generated when ozone was added to a 1 m^3 glass chamber that contained either pine shelving, oriented strand board (OSB), beech boards, or beech boards painted with an “eco” paint. Their experiments demonstrated that the emission of terpenes and potential generation of SOAs varied greatly among different types of wood and pressed wood materials. In the case of the pine boards and painted beech boards, the SOAs concentrations generated at modest ozone concentrations approached or exceeded current guideline levels for $PM_{2.5}$ (particulate matter with <2.5 μm in size) established by the United States Environmental Protection Agency (U.S.EPA) and the World Health Organization (WHO). It should be noted that more than 50% of the initial mass increase resulting from indoor terpene/ozone reactions is in the ultrafine mode. Inhaled ultrafine particles have high deposition in the human respiratory tract. There is increasing evidence that these ultrafine particles affect the human pulmonary, cardiovascular, and even the central nervous system. Furthermore, indoor-generated secondary particles are different to those outdoors owing to the different sources and formation processes. For example, outdoor SOAs are typically exposed to sunlight and the absorption of UV radiation by the particles results in the rapid photolysis and degradation of SOA compounds such as organic peroxides (Walser et al., 2007). These photochemical aging processes are slower or even suppressed in indoor environments, and consequently particle-bound reactive species such as the peroxides could penetrate into the lungs and deliver oxidative stress to the tissue (Chen and Hopke, 2009). Much of the surface of indoor-generated particles could be nitrated or acidic in nature.

However, the formation of indoor SOAs varied under certain conditions, for example, with particular physical parameters such as air exchange rate (ACH), relative humidity (RH), and temperature (T). Diurnal or seasonal variations of these physical parameters could dramatically influence the generation and growth of indoor SOAs (von Hessberg et al., 2009). Additionally, the concurrent gaseous pollutants such as ammonia (NH_3) can also affect the formation and growth of SOAs indoors. For example, temperature was found to have a dramatic effect on SOAs formations from two ozonolysis systems, cyclohexene and α-pinene. Isothermal experiments were conducted for both systems where the lowest temperature, 278 K, formed approximately 2.5-3 times and 5-6 times the SOA formed at 300 K and 318 K respectively (Warren et al., 2009). As reported by Fadeyi et al.(2009), the SOA number and mass concentrations at a recirculation rate of 14 h^{-1} were significantly smaller than at a recirculation rate of 7 h^{-1} for otherwise comparable conditions. Na et al. (2007) examined the influence of ammonia on SOAs growth after the reaction from the α-pinene/ozone oxidation system under dry and humid conditions. Number and volume concentrations quickly increased within the reactor by 15% and 18% respectively, when NH_3 was added after the reaction between terpene and ozone ceased.

It should be emphasized that previous studies only focused on individual BVOC and how physical parameters influenced their reaction with ozone in a small chamber (i.e., <1 m^3 in volume). Actually, in real indoor environments, the indoor BVOCs are mixtures rather than single compound. Forester and Wells (2011) reported that the BVOCs mixtures react differently with ozone in compassion with reactions between individual components and ozone. Therefore, studies focusing on individual BVOC chemistry may not fully reflect the reality for indoor environments because a mixture of different reactive BVOCs can be emitted from household cleaning products. However, few systematic studies have been done on the effect of these parameters including ACH, T, RH, and the co-existence of NH_3 on the formation and growth of SOAs from reaction between emissions of floor cleaners, air fresheners and ozone.

1.2 Objectives of Study

The aim of this study is to investigate ozone-initiated formation of indoor secondary organic aerosols with emissions from cleaning products and air fresheners in Hong Kong in a large environmental chamber. Solid-phase microextraction (SPME) coupled with the gas chromatography/mass spectrometry (GC/MS) method was firstly optimized and it was then applied in analyzing BVOCs components in cleaning products and air fresheners popularly used in Hong Kong. Effect of physical parameters including ACH, T, RH, and concurrent NH_3 on the formation of indoor secondary pollutants with emissions from routinely used household cleaning products in the presence of ozone was studied. The specific objectives of this study are as follows:

i) To develop and optimize the sampling and analytical parameters of the SPME-GC/MS method for indoor BVOCs analysis;

ii) To determine the concentrations of BVOCs components in household cleaning products and air fresheners popularly used in Hong Kong;

iii) To evaluate the influences of ACH, T and RH on secondary pollutants formation (SOAs and carbonyl compounds) from the ozonolysis of BVOCs emitted by cleaning products;

iv) To investigate the impact of coexistent NH_3 on secondary pollutants formation from the ozonolysis of BVOCs emitted by cleaning products.

Chapter 2 Literature Review

2.1 Indoor biogenic volatile organic compounds (BVOCs)

2.1.1 BVOCs: definitions and indoor sources

In the last two decades, biogenic volatile organic compounds (BVOCs) in indoor environments have attracted more and more attention because of their ubiquitous existence. BVOCs are hydrocarbons of biological origin which mainly include isoprene and monoterpenes (Kesselmeier and Staudt, 1999). The carbon skeletons of terpenes are derived from isoprene (C_5H_8) unit and thus it can be subdivided into monoterpenes (C_{10}), sesquiterpenes (C_{15}), diterpenes (C_{20}), sesterterpenes (C_{25}), and polyterpenes (C_{5n}) (IUPAC, 1997). Due to their pleasant smell, BVOCs, especially monoterpenes and oxygenated monoterpenes, are extensively used as ingredients in many household products, particularly in cleaning products and air fresheners (Singer et al., 2006b). Terpenes are also widely used in solvents, paintings, deordorants, and varnish. However, the presence of unsaturated carbon double bonds within the molecular structures of BVOCs makes these compounds highly reactive with indoor oxidants such as ozone, hydroxyl radicals, and nitrate radicals that can eventually lead to the formation of various secondary pollutants.

Singer and coworkers (2006) conducted experiments to quantify emissions and concentrations of terpenoids from cleaning products and air fresheners used in a 50 m^3 room with air exchange rate of 0.5 h^{-1}. It was found that after the full-strength application of pine-oil cleaners, the 1-h concentrations for α-terpinene, d-limonene, terpinolene, and α-terpineol were 90-120, 1000-1100, 900-1300 and 260-700 $\mu g/m^3$ respectively. Good correlation was also found between the abundances of BVOCs collected in a university building and the frequency of cleaning activities, which suggested that the use of household cleaning reagents could pose residential occupants on high pollutant level exposure (Solomon et al., 2008). Their studies showed that air pollutants emitted from cleaning products and indoor building materials, including monterpenes, aldehydes and acetone, exhibited general trends of higher concentrations indoors compared to the outdoor level; indoor VOCs concentrations were found to be 2-10 times higher in weekdays as compared with those at the weekend.

BVOCs such as d-limonene and α-terpineol were also identified from materials for flooring installation (Wilke et al., 2004). In the study conducted by Kwon et al. (2008) focusing on evaluating the emission composition for 42 liquid household products (including deodorizers, household cleaners, color removers, pesticides, and polishes) sold in Korea, d-limonene was identified as having the highest occurrence (76.2%) in the household products. The emissions composition for selected household products sold in Korea was analyzed by using headspace analysis;

BVOCs species such as d-limonene and α-pinene were found with an occurrence frequency up to 44.2% and 18.6% respectively (Kwon et al., 2007a). The direct characterization of BVOCs components in household products can provide valuable information for the estimation of inhalation exposure and for the selection of safer consumer products for residential occupants and occupational cleaning staff.

In order to reduce the potential health risk posed on building occupants and cleaning personals, regulations to control VOC emissions from household products have been established by several governmental authorities such as United States Environmental Protection Agency (U.S.EPA), the California Air Resources Board (CARB) and the Hong Kong Environmental Protection Department (HK EPD) (CARB., 2009; HKEPD, 2007; USEPA, 1998) . For example, the VOC content limits (weight-percent VOC) in air fresheners (single-phase aerosol) regulated by CARB, US EPA and HK EPD were 30%, 70% and 30% respectively.

2.1.2 Analytical methods for BVOCs

Measurement of airborne BVOCs in both outdoor and indoor environments is of great interest because of their ubiquitous presence. BVOCs emitted from vegetation can contribute to the formation of tropospheric ozone and the production of SOAs and thus influence the atmospheric chemistry (Atkinson and Arey, 2003b; Lee et al., 2006). In indoor environments, these compounds can react rapidly with ozone, producing formaldehyde, hydrogen peroxide, hydroxyl radical and secondary organic aerosols (SOA) and imposing various adverse effects on human health. Monoterpene is one of the most dominant classes of BVOCs (Kesselmeier and Staudt, 1999). A few studies demonstrated that BVOCs are present in cleaning products and air fresheners of high concentrations. These products are regularly used indoors for hygiene purposes (Singer et al., 2006b). The possibility of the formation of secondary organic pollutants from reactions between constituents of household products and ozone has been widely evidenced (Coleman et al., 2008; Destaillats et al., 2006).

It is thus important to characterize and quantify BVOCs composition profiles of cleaning products in order to understand the role of terpenoids in indoor chemistry. Detecting highly reactive indoor volatile compounds, such as terpenes and oxygenated terpenes, is a challenging task in environmental monitoring studies. Traditionally, solid adsorbents including porous organic polymers (e.g., Tenax TA and Tenax GR) or carbon-based materials (e.g., Carbotrap and Carbograph) are widely used to collect airborne BVOCs, and these collected samples will then be thermally desorbed and analyzed with a gas chromatograph (Ortega and Helmig, 2008). The use of electro-polished stainless steel canisters has also demonstrated the feasibility in collecting BVOCs. The whole air samples are commonly analyzed using cryo-focusing followed by GC with flame ionization detector (GC/FID) or mass selective detector (GC/MS) (Pressley et al., 2004). However, the stability of these highly reactive compounds to survive these sampling processes is questionable. Furthermore, both solid sorbents and canister apparatus require the use of specific and expensive analytical equipment (i.e. thermal desorption and cryo-focusing units). Compared with solvent extraction, thermal desorption advances desorption efficiencies and avoids unnecessary sample dilution, leading to an increase of analytical sensitivity (Dorothea et al., 2006).

Solid-phase microextraction (SPME), which is a solvent-free sample preparation technique that integrates sampling, isolation and concentration for the analysis complying with traditional chromatographic separation and detection methods, was studied intensively as an alternative method recently. Currently, SPME method has been widely applied to the sampling and analysis of environmental samples (Adam et al., 2005; Bouvier-Brown et al., 2007; Nicolle et al., 2008; Zeng et al., 2008), pharmaceutical(Camarasu et al., 2006), and food samples (Lambropoulou and Albanis, 2003). For example, Adam et al.(2005) used a headspace solid-phase microextraction procedure based on three commercial fibers (100 μm polydimethylsiloxane, 65 μm polydimethylsiloxane–divinylbenzene and 50/30 μm divinylbenzene–Carboxen–polydimethylsiloxane) to determine essential oils in dried leaves of yacon. The extraction performance of these compounds with different SPME fibers was compared. The results showed that 30/50 μm DVB–CAR–PDMS fibre gave the best combination of sensitivity fulfilling the requirements of the method for yacon analysis on the target compounds. Emissions from living plants have been sucessfully monitored using SPME (Bouvier-Brown et al., 2007; Zini et al., 2001). Bouvier-Brown et al. (Bouvier-Brown et al., 2007) quantified sesquiterpene and oxygenated terpene emissions from live vegetation by using solid-phase microextraction fibers (polydimethylsiloxane–divinylbenzene (PDMS/DVB)). The experimental conditions and procedures for field collections followed by laboratory analysis were optimized. Results showed that concentrations determined by SPME fibers agreed with meansurements made using proton transfer reaction mass spectrometry (PTR-MS) within the estimated error of the method for well calibrated compounds. SPME has been explored in indoor air monitoring. Wei and co-workers reported the preparation of a SPME fiber coated with gamma-Al_2O_3 to determine volatile organic compounds in indoor air (Wei et al., 2004). Larroque et al (2006) developed an analytical methodology associated with an adsorptive PDMS/Carbon fiber to determine 10 representative VOCs in indoor environments. Linear calibration curves were up to 10 μmol m^{-3} for all the compounds with correlation coefficients above 0.99. The analytical reproducibility varied from 6 to 12%. This optimized method was successfully applied to determine VOCs content in classrooms in two schools. More recently, the emission of low molecular weight compounds from recycled high-impact polystyrene has been investigated using headspace SPME (HS-SPME) and GC/MS (Vilaplana et al., 2009). Target compounds including styrene, benzaldehyde, acetophenone, and 2-phenylpropanal were selected for the optimization of the HS-SPME sampling procedure.

2.2 Indoor ozone: sources and typical concentrations profiles

Tropospheric ozone is mainly formed from photochemical reactions. The formation of troposhperic ozone occurs when nitrogen oxides (NO_x) and hydrocarbon compounds react in the atmosphere in the presence of UV sunlight. The common emission sources of hydrocarbon include vehicle exhaust, industrial emissions, petroleum-based fuel and organic solvents. Stratospheric ozone (commonly referred to as the ozone layer) results primarily from the interaction of UV light with oxygen in the upper atmosphere (Spengler et al., 2004). In general, ozone is a relatively stable compound, but it can be decomposed into oxygen at high concentrations or elevated temperatures. Since ozone is a very strong oxidizing agent, it is potentially deleterious to human health. In order to protect the health of citizens, many government organizations have established regulations on ozone concentration in the air. For example, the recommended 8 h-average ozone concentration by World Health Organization is 60 ppb (WHO., 2000).

Ozone in indoor environments can come from outdoor air due to air exchanging with outdoors (Weschler, 2000b). In an ozone exposure study carried out by Romieu et al. (1998) in Mexico City, it was found that indoor ozone levels were 10-30% of the outdoor ozone concentrations and the mean indoor-to-outdoor ratio was 0.20 (SD=0.18). Indoor ozone concentrations can be a significant fraction of those outdoors depending on the different ventilation rates. The measurements conducted by Jakobi and Fabian in various kinds of non-air-conditioned rooms demonstrated that maximal indoor ozone concentrations were 80% of those outdoors(Jakobi and Fabian, 1997). The average indoor/outdoor ratio of ozone was 0.5 as demonstrated in the study. In addition, several types of office equipment were known to generate ozone such as air purifiers, dry-process photocopy machines, photocopiers, and laser printers (Britigan et al., 2006; Hubbard et al., 2005; Leovic et al., 1996). Britigan et al. (2006) investigated several types of air purifiers' ozone production ability in different indoor environments with RH of 40-50%. Office rooms, bathrooms, bedrooms, and cars were selected as typical test rooms. It was found that O_3 concentrations well exceeded public and/or industrial safety levels established by U.S. Environmental Protection Agency, California Air Resources Board, and Occupational Safety and Health Administration in most cases. Hubbard et al. (2005) assessed the effects of an ozone generator on indoor secondary organics aerosol concentration in actual residential settings and results suggested that ozone generators in the presence of terpene sources can facilitate the growth of indoor fine particles in residential indoor atmosphere. Electrostatic air filters and electrostatic precipitators can also generate ozone.

Some studies also identified the ozone concentrations in aircraft (Wisthaler et al., 2005). Spengler et al. (2004) studied the time-integrated ozone levels on 106 flight segments using passive samplers. Two different sampling time intervals were examined including from taking off to landing. Some of these aircraft contained catalytic ozone converters to remove ozone from the airstream. However, the 145 time-integrated average ozone concentrations on these flights was 80 ppb (with a standard deviation of ±30 ppb); and 20% of the measurements exceeded 100 ppb and 11% exceeded 120 ppb.

Indoor ozone concentration depends on various factors, such as the outdoor ozone concentration, the rate at which indoor air is exchanged with outdoor air, indoor sources of ozone, the rate of which ozone is removed by indoor surfaces, and reactions between ozone and other chemicals in the air. Indoor ozone is not only a health concern, but also adversely affects materials, pigments, and cultural artifacts (Weschler, 2000b). Furthermore, ozone is a major driver of indoor chemistry. The products generated from ozone-initiated indoor chemistry can be more irritating, odorous, and damaging to materials than their precursors. It was estimated that daily inhalation intakes of indoor ozone contributed 25-60% to the total daily ozone intake (Weschler, 2006). Therefore, indoor ozone exposure represents a major fraction of total ozone exposure for humans.

2.3 Indoor gas-phase chemistry: formation of secondary organic aerosols (SOAs) and gaseous pollutants

BVOCs in indoor environments can react with oxidants resulting in the formation of secondary pollutants such as secondary organic aerosols and secondary gaseous pollutants. Ozone is a common initiator for indoor gas-phase oxidation chemistry. Hydroxyl radicals (OH) and nitrate radicals (NO_3) can also be at sufficient high concentrations resulting in the formation of secondary pollutants indoors (Nazaroff and Weschler, 2004). Generally, indoor hydroxyl radicals are derived dominantly from ozone/alkene reactions (Weschler, 2000a), while indoor nitrate radicals result from the reaction between ozone and nitrogen dioxide (Nazaroff and Cass, 1986).

SOAs formation from ozone-initiated reactions with BVOCs has been widely studied in atmospheric chemistry. However, those studies have uncertain direct applicability for elucidating SOAs formation indoors because there is no photochemistry involved for indoor SOAs formation. Furthermore, indoor generated secondary particles are different to those outdoors owing to the different sources and formation processes. For example, outdoor SOAs are typically exposed to sunlight and the absorption of UV radiation by the particles results in the rapid photolysis and degradation of SOA compounds such as organic peroxides (Walser et al., 2007). These photochemical aging processes are slower or even suppressed in indoor environments. The consequently particle-bound reactive species such as the peroxides could penetrate into the lungs and deliver oxidative stress to the tissue (Chen and Hopke, 2009). Much of the surface of indoor generated particles could also be nitrated or acidic in nature.

Several studies have measured SOAs formation and growth from ozone reactions with pure terpenes or with emissions from terpene-containing products under indoor-relevant conditions. For example, a significant degree of secondary particle growth was observed immediately upon mixing of household products and ozone in the chamber (Destaillats et al., 2006). Toftum et al. (2008) examined the formation and growth of SOAs generated when ozone was added to a 1 m^3 glass chamber that contained either pine shelving, oriented strand board (OSB), beech boards, or beech boards painted with an "eco" paint. Their experiments demonstrated that emissions of terpenes and potential generation of SOAs varied greatly among different types of wood and pressed wood materials. In the case of the pine boards and painted beech boards, the SOAs concentrations generated at modest ozone concentrations approached or exceeded current guideline levels for $PM_{2.5}$ (particulate matter with <2.5 μm in size) established by the United States Environmental Protection Agency (U.S.EPA) and the World Health Organization (WHO).

The studies carried out by Aoki and Tanabeb (2007) showed that the combination of ozone and different building materials in test chambers produced significant increases in the number concentration of sub-micron particles. In their study, building materials such as wooden boards, rubber adhesives and plastic tile with floor wax were selected. Coleman et al. (2008) analyzed secondary organic aerosols (SOAs) data from a series of small-chamber experiments in which terpene-rich vapors from household products were combined with ozone under conditions analogous to product use indoors. In each of the 16 experiments, a burst of particle formation by nucleation occurred immediately after ozone addition.

As demonstrated by Fan et al. (2005), the reactions of O_3 with the two terpenes were the key processes contributing to the formation of hydroperoxides and ultrafine particles in the O_3/23 VOCs system. The formation of ultrafine particles produced by ozone/limonene reactions in indoor air under low/closed ventilation conditions was observed and it was found that an excess of O_3 tended to give higher maximum particle concentrations (Langer et al., 2008). D-limonene secondary ozonides (SOZ) were detected from the reactions between d-limonene and ozone; and these compounds were quite stable in dry and humid air without oxidants (Nojgaard et al., 2007). Furthermore, the d-limonene/ozone ratio was observed to be crucial for the stability of the SOZ because it is prone to ozonolysis. No SOZ could be detected in completely reacted 1:1 mixtures. Sarwar et al. (2003) assessed the effects of limonene/O_3 reactions on indoor secondary organic particles and the results clearly demonstrated that fine particle formation/growth can occur when both limonene and O_3 are present in indoor environments at elevated levels. Their results suggest that O_3 reactions with limonene can lead to elevated exposure to particles with diameters less than 1.0 μm.

Weschler and Shields (1999) studied the effects of reactions between ozone and selected terpenes on the concentrations and size distributions of airborne particles in a typical indoor setting. The study was conducted in adjacent and identical offices. It was found that the number of particles in the 0.1-0.2 μm diameter size range was as much as 20 times larger in the office with deliberately supplemented ozone and d-limonene than in the office serving as control. Hubbard et al. (2005) investigated the effects of an ozone-generating air purifier on indoor secondary particles in three residential dwellings. Results indicated that ozone generators in the presence of terpene sources facilitated the growth of indoor fine particles in residential indoor atmosphere. Human exposure to secondary organic particles can be reduced by minimizing the intentional release of ozone, particularly in the presence of terpene sources. Field studies also confirmed the formation of SOAs in indoor environment. Morawska et al. (2009) investigated ultrafine particles in primary school classrooms in relation to classroom activities. Significant increases of ultrafine particles concentration occurred during cleaning activities when detergents were used.

Besides the formation of SOAs from ozone initiated indoor chemistry, several dicarbonyl products such as glyoxal, methylglyoxal, and 4-oxopentanal were quantified from the gas-phase reactions of the hydroxyl radical and ozone with limonene, α-terpineol, and geraniol (Forester and Wells, 2009). Total carbonyl yields ranged from 5.1% for the limonene/O_3 reaction to 92% for the geraniol/O_3 reaction. A small amount of ketones formation was detected and quantified from the reactions of ozone with gas-phase primary emissions from carpets (Morrison and Nazaroff, 2002). Acetone, glyoxal, and 2-oxopropanal were identified from the α-terpineol/OH reaction products, while 2-oxopropanal was identified from α-terpineol/O_3 reaction products (Wells, 2005). Hydroxyl radicals (OH) can also be produced from the reactions of O_3 with certain alkenes such as d-limonene, α-terpinene, and α-pinene (Weschler and Shields, 1996). Wisthaler et al. (2005) examined secondary gaseous products formed when ozone reacted with the materials in a simulated aircraft cabin by using proton-transfer-reaction mass spectrometry (PTR−MS). The concentration of VOCs increased from 35 ppb to 80 ppb after the addition of ozone to the cabin without T-shirts, whereas the combination of soiled T-shirts and ozone increased the mixing ratio of detected pollutants to 110 ppb (Wisthaler et al., 2005). During the reaction of ozone and limonene, gaseous byproducts including formaldehyde and formic acid were detected (Zhang et al., 1994). Field experiments were conducted in four homes during summer to quantify ozone-induced secondary emission rates (SERs) of aldehydes on indoor surfaces (Wang and Morrison, 2006). Four surfaces in each house were examined: living room carpet, living room wall, kitchen floor, and kitchen counter. Upon exposure to ozone for 3 hours, formaldehyde and C_3-C_{10} saturated aldehydes, especially nonanal, were emitted as products of ozone-surface reactions.

Recently, thirdhand smoke (THS) has been recognized as a contributor to indoor pollution due to the role of indoor chemistry occurred on indoor surfaces (Petrick et al., 2011). Environmental tobacco smoke (ETS) consists of a complex mixture of gaseous and particulate pollutants produced from the sidestream and diluted exhaled mainstream smoke from the combustion of tobacco products. It was found that SOA formation from the sorbed nicotine-ozone reaction varied in size distribution and particle number concentration with different RH and substrate types. Because of the toxicity of reaction byproducts and that ultrafine particles may contribute to adverse health effects, it is possible that exposure to THS ozonation products may pose additional health risks on residents. The study carried out by Sleiman et al. (2011) showed that residual nicotine from tobacco smoke sorbed to indoor surfaces can react with ambient nitrous acid (HONO) to form carcinogenic tobacco-specific nitrosamines (TSNAs). It was revealed that the formation of TSNA was fast with up to 0.4% conversion of nicotine. Considering the adsorption/absorption of nicotine released from ETS on indoor surfaces including clothing and human skin, these results indicated an unappreciated health hazard.

2.4 Effect parameters on indoor SOAs formation

Indoor SOAs are formed from gas-phase oxidation of anthropogenicall or naturally emitted VOCs, especially unsaturated VOCs such as BVOCs. The oxidation processes generally produce lower vapor pressure of secondary pollutants. The species can lead to new ultrafine particle formation or condense on preexisting particles in the indoor environment. The indoor gas-phase reactions can be affected by various factors in real indoor environments. Factors including T, RH, ACH, concurrent gaseous pollutants (i.e., NH_3, SO_2 and $NO_{x,}$) and nucleation seeds (i.e., primary particulate matter) can affect the formation and growth of SOA indoors.

2.4.1 Effect of physical parameters

The formation of indoor SOAs occurred under certain conditions, for example, with particular environmental parameters such as air exchange rates (ACH), relative humidity (RH), and temperature (T). SOAs can be formed only when the chemical reaction rates are comparable to ventilation rates because sufficient time is needed for pollutants reaction (Weschler, 2000a). The residence time of pollutants indoors is mainly determined by ventilation. Indoor pollutants can react with oxidants such as ozone to generate secondary pollutants with longer residence time. On the other hand, the initial precursors' concentrations can be diluted with higher ventilation rate. Although the elevated ventilation rate can dilute precursor pollutant concentrations, it can also increase ozone infiltration from outdoors to indoors (Fadeyi et al., 2009). As reported by Fadeyi et al. (2009), the SOA number and mass concentrations at a recirculation rate of 14 h^{-1} were significantly smaller than at a recirculation rate of 7 h^{-1} for otherwise comparable conditions. Therefore, the impact of ventilation rates on indoor chemistry is a much more complex process.

A few chamber studies demonstrated that T has a pronounced influence on the mass and number concentrations of SOAs generated from the reactions between BVOCs and ozone (Jonsson et al., 2008; Lamorena and Lee, 2008; Pathak et al., 2007; Saathoff et al., 2009; Svendby et al., 2008; Takekawa et al., 2003; von Hessberg et al., 2009). Based on indoor chemistry and exposure model predication, indoor secondary organic aerosol number concentrations are expected to increase by a factor of two for every 10 °C decrease in indoor temperatures (Takekawa et al., 2003). Saathoff et al. (2009) investigated the SOA formation as a function of temperature for the ozone-initiated reaction of α-pinene and limonene. The SOA yields increased by up to a factor of approximately 5 to 10 for α-pinene and by a factor of 2.5 for limonene from 313 to 243K and 313 to 253 K. The studies carried out by Jonsson et al. (2008) demonstrated that SOAs formation from ozonolysis of α-pinene and Δ^3-carene exhibited a similar temperature dependence regarding both particle number and mass concentrations, whereas that of limonene showed a different dependence.

Pathak et al. (2007) investigated the effect of temperature on SOAs mass fractions (or yields) from the ozonolysis of α-pinene in a temperature controlled smog chamber. Experiments were performed with and without ammonium sulfate aerosol seeds at RH < 10% and at 0 ^{o}C, 15 ^{o}C, 20 ^{o}C, 30 ^{o}C and 40 ^{o}C, respectively. It was found that secondary organic AMFs from the ozonolysis of α-pinene present a weak dependence on temperature in the 15 ^{o}C to 40 ^{o}C range but stronger temperature dependence in the 0 ^{o}C and 15 ^{o}C range. With the semi-empirical thermodynamic approach, the productions of SOAs increased with decreasing T because of partitioning to the condensed phase (Jonsson et al., 2008; Odum et al., 1996; Pankow, 1994, 2007). The T can affect complicatedly on the SOAs' reaction pathways and its degree of influences varied in different environmental systems. Enthalpy of precursor vaporization was found to significantly impact T dependence on the SOA formation. Sheehan and Bowman (2001) studied the temperature-dependence of SOA concentrations by using an absorptive-partitioning model under a variety of simplified atmospheric conditions. Assuming variation of vapor pressures with temperature to be the main source of temperature effects, results showed that temperature was likely to have a significant influence on SOA partitioning and resulting SOA concentrations. The amount of SOAs formed at 17 ^{o}C was approximately 5-6 times higher than that at 45^{o}C during the ozonolysis of α-pinene (Warren et al., 2009).

RH is another critical physical parameter dramatically influencing the SOA formations. Jonsson et al. (2008) reported that water effect at a low T (-30 ^{o}C) could be ascribed to physical uptake and cluster stabilization, while at higher T (0 and 25 ^{o}C) chemical reaction mechanism could also be altered. In von Hessberg et al. (2009) about temperature dependence of the SOA formation from the ozonolysis of β-pinene, the SOA yields increased with inverse temperature under dry conditions, while the SOA yields exhibited a linear decrease with inverse temperature under humid conditions. Cocker et al. (2001) investigated the effect of RH on gas-particle portioning of SOA of the α -pinene/O_3 system in the presence of ammonium sulfate (aqueous, dry), ammonium bisulfate seed (aqueous, dry), and aqueous calcium chloride seed aerosols. The yield of SOA varied little with RH, and was not affected by the presence of dry inorganic salt aerosols, while the yield of SOA was reduced in the presence of aqueous salt aerosols. Furthermore, it was found the degree of reduction was electrolyte dependent, with aqueous ammonium sulfate leading to the largest reduction and aqueous calcium chloride the smallest. Jonsson et al. (2006) examined the effect of water on the initial SOA formation from gas-phase ozonolysis of limonene, Δ^3-carene, and α-pinene. Results showed that an enhancement in water vapor concentration caused an increase in both particle mass and total number concentrations. The effect on number and mass was a factor of 2-3 and 4-8 respectively. It was concluded that low volatility products were probably produced from gas-phae reaction with an increase in water concentration. The chemical compositions of SOAs formed from the ozonolysis of 1-tetradecene in humid and dry air was also different indicating different reaction pathways under different RH (Tobias et al., 2000).

2.4.2 Effect of coexistence of chemical pollutants

The effect of nitrogen dioxide (NO_2) on SOA formation from the ozonolysis of α-pinene and d-limonene indoors were investigated and it was found that particle formation ability was significantly reduced because of the loss of O_3 in the presence of NO_2 in the reaction systems (Nojgaard et al., 2006). The presence of NO_2 introduced an additional loss term for O_3 resulting in the formation of nitrate radicals and this affected particle formation since the nucleation potential of NO_3 is much lower than that of O_3. Ng et al. (2007) investigated the effect of NO_x on SOA formation from the photooxidation of α-pinene under varying NOx conditions. It was observed that the SOA yields decreased as NO_x level increased. Song et al. (2005) also observed that the SOA yields from the ozonolysis of m-xylene and toluene decreased with higher NO_x concentrations.

Na et al. (2007) investigated the effect of ammonia (NH_3) on SOA formation from the ozonolysis of α-pinene under dry and humid conditions. An increase of particle number and volume concentrations by 15% and 18% was observed when NH_3 was added after the reactions between α-pinene and ozone ceased. It was assumed that NH_3 can react with organic acids which were generated from the oxidation processes resulted in the formation of new particles. Another assumption is that the initial presence of NH_3 can significantly enhance aerosol yields in α-pinene/ozone reactions regardless of the presence of water vapor. The role of NH_3 on SOA formation in the dry and humid conditions was discussed in a theoretical modeling study. Based on the results obtained in their study, it can be speculated that gas phase organic acids could be converted into condensable salts by reacting with NH_3. An opposite result was found by another study in which aerosol yields were significantly reduced after the addition of NH_3 to the styrene/ozone system. This can be ascribed to the rapid decomposition of intermediates (Na et al., 2006).

2.5 Potential health risks posed by secondary pollutants from indoor gas-phase chemistry

Exposure to indoor ozone and its oxidation products has some indirect connections with morbidity/mortality as indicated in many studies. Strong associations were found between outdoor ozone and mortality in cities where the transport of ozone from outdoors to indoors was greater (Weschler, 2006). It was estimated that daily inhalation intakes of indoor ozone accounted between 25 and 60% of total daily ozone intake. Additionally, some of the ozone-initiated oxidation products, including formaldehyde, acrolein, hydroperoxides, fine and ultrafine particles, are known or suspected to adversely affect human health. Generally, more than 50% of the initial particle mass increase resulting from indoor terpene/ozone reactions is in the ultrafine mode. There is increasing evidence that these ultrafine particles affect the human pulmonary and cardiovascular systems, and even the central nervous system because these formed ultrafine particles have high deposition in the human respiratory tract. Some of the products of indoor reactions are highly reactive, such as Criegee biradicals, nitrate radicals and peroxyacyl radicals. These reactive species can result in the formation of other reactive species such as hydroxyl, alkyl, alkylperoxy, hydroperoxy and alkoxy radicals (Weschler, 2000a).

The study carried out by Tamas et al. (2006) demonstrated that the products generated from ozone-initiated reactions with limonene negatively affect short-term evaluations of perceived air quality (PAQ). Wolkoff et al. (2000) established relationships between no-observed-effect-levels (NOELs) and concentration-effect of highly irritating substances in reactions of ozone with terpenes. It was found that reaction mixtures of excess terpene and ozone considerably below their NOEL concentrations can result in significant upper airway irritation. Mixing VOCs with O_3 was shown to produce irritating compounds including aldehydes, hydrogen peroxide, organic acids, secondary organic aerosols, and ultrafine particles (particulate matter with aerodynamic diameter < 0.1 μm) (Fiedler et al., 2005). Rohr et al. (2002) evaluated the effects of oxidation products of ozone and the unsaturated hydrocarbons d-limonene, α-pinene, and isoprene on the upper airways, the conducting airways, and the lungs over a longer exposure period. Findings suggested that the terpen/ozone reaction products may have moderate-lasting adverse effects on both the upper airways and pulmonary regions. This may be important in the context of the etiology or exacerbation of lower airway symptoms in office workers, or of occupational asthma in workers involved in industrial cleaning operations.

Nojgaard et al. (2005) investigated the exposure to limonene oxidation products (LOPs) and the terpene oxidation product methacrolein at ppb levels using blink frequency (BF) as a measure of trigeminal stimulation of the human eye. Results showed that mean BF increased significantly during exposure to LOPs and methacrolein in comparison with the baseline of clean air. The findings obtained coincided with weak eye irritation symptoms. Kleno and Wolkoff (2004) investigated changes in eye blink frequency as a measure of trigeminal stimulation by exposure to limonene and isoprene oxidation products, and nitrate radicals. The mean blink frequency increased significantly during subjects' exposure to gas-phase oxidation products of limonene and isoprene at lower ppb levels of LOPs, 42% ($P<0.0001$) and NO_3, 21% ($P<0.022$), compared with that at baseline (Kleno and Wolkoff, 2004). Wilkins et al. (2003) studied the effects of reaction time, relative humidity and initial ozone concentration on irritant formation in a flow reaction system with limonene and isoprene as reaction precursors. Upper airway irritation was measured in mice as reduction of the respiratory rate. For both BVOCs, the maximum irritation was observed at low humidity (< 2% RH)/short time (16-30 s) reaction mixtures, while both moderate humidity (similar to 32% RH) and longer reaction time (60-90 s) led to significantly less irritation.

Hence, it is important to study the influence parameters on indoor secondary pollutants formation from ozonolysis processes. Studies focusing on individual BVOC chemistry may not fully reflect the reality for indoor environments because a mixture of different reactive BVOCs can be emitted from household cleaning products. However, few studies have been done on the effect of these parameters on the formation of secondary pollutants from reactions between ozone and emissions of household cleaning products and air fresheners. Therefore, it is significant to have a detailed examination on BVOCs components in household cleaning products and air fresheners, and the effect of physical parameters including ACH, T, RH, and concurrent gaseous pollutants such as NH_3 on the formation of indoor secondary pollutants with BVOCs emissions from routinely used household cleaning products in the presence of ozone.

Chapter 3 Methodology

3.1 Large environmental chamber

In this study, the effect of physical parameters including ACH, T, and RH, and concurrent ammonia (NH_3) on secondary pollutants formation from the ozonolysis of BVOCs emitted from cleaning products including floor cleaners, kitchen cleaners and dishwashing detergents were investigated in a large environmental chamber (Figure 3-1). The large environmental chamber was made of stainless-steel (3.2 m × 3.2 m × 2.5 m) with an effective volume of 18.26 m^3 (Lee and Wang, 2006). Its surface area to the volume ratio was 2.87 (m^2/m^3). Figure 3-2 shows the schematic diagram of the large environmental chamber set-up. Clean air was supplied to the chamber by drawing outside air through an air cleaning system with activated charcoal particle filters to remove gaseous organics and High-Efficiency Particulate Air (HEPA) filters to remove particles. Mixing fans were installed at the ceiling of the chamber to ensure homogeneous mixing. The chamber system has a central control system for adjustment of ACH, RH and T. The ACH was pre-determined by the first-order decay of SF_6, which was introduced to the chamber and continuously monitored with a Photoacoustic Field Gas Monitor (INNOVA 1412, Santa Clara, CA). The ACH was altered by controlling the airflow rate. The T of air was controlled by conditioning coils. RH was regulated by adding an appropriate amount of deionized water into the air system. A Q-Trak monitor (Model 8550, TSI Inc., Shoreview, MN) recorded both T and RH continuously in a 1 minute-sampling interval. Prior to use, the chamber was fully cleaned by scrubbing the interior surfaces with a sponge mop. Before each experiment, the chamber was conditioned for 4 hours at the desired physical conditions. The background in the chamber air were kept <10 μg m^{-3} for total volatile organic compounds (TVOCs) and < 2 μg m^{-3} for individual VOCs (Lee and Wang, 2006; USEPA., 1999b).

3.2 Sampling methods and Analysis of target pollutants

3.2.1 VOCs sampling and analysis

BVOCs were sampled with the solid-phase microextraction (SPME) method. A manual SPME sampling holder consists of a 75 μm Carboxen-PDMS fiber (Supelco, Bellefonte, PA). New fiber was heated in a gas chromatography (GC) injection port (6890 GC, Hewlett-Packard, Santa Clara, CA) under continuous helium (He) gas flow at 300°C for 1 hour, aiming to thermally desorb any impurities. The conditioned fibers were stored properly inside a clean box in laboratory. Before sample collection, each fiber was re-conditioned in the GC injection port at 300 °C for 10 minutes. Experimental results showed that no significant amount of BVOCs remained on the fiber. For sample collection, the fiber was inserted through the sampling port and exposed for 5 minutes in the chamber. Once the sampling was completed, the fiber was stored and then inserted into the GC injection port at 280°C for 4 minutes. During the desorption period, the GC oven temperature was kept at 50°C. Such a temperature condition would allow the analytes released from the SPME fiber on the head of the GC column in a narrow band. The injector was kept in the splitless mode for the first 2 minutes and then switched to the split mode until the end of the GC oven temperature program. The GC oven temperature program then started at 50 °C and was held at this temperature for 3 minutes; it was then ramped at a rate of 5°C/minutes to 95°C and 10°C/minutes to 130°C and 55 °C/minutes to 290 °C, and was held at the final temperature of 290 °C for 3 minutes. A DB-5MS UI column (J&W, Agilent Technologies, Inc., Santa Clara, CA, 30 m × 25 mm i.d. × 25 μm film thickness) was adopted for the analytes separation. The GC injector temperature was kept at 280°C throughout the analysis. The carrier gas was He (ultra-high purity grade) held at a constant flow of 1.0 ml/min. The analytes after the GC separation were detected using an MS (5973 MS, Hewlett-Packard), which was operated at an ion source temperature of 230 °C and 70 eV for electron ionization (EI). The mass scan range was from 50 to 200 amu. Identification was achieved by comparing the mass spectra with NIST 08 MS library and retention time of the chromatographic peaks with those of calibration standards. The two or three most abundant ion fragments of each BVOC were selected as extract ions for the quantification. The high-purity chemical standards including α-pinene, camphene, β-pinene, myrcene, 3-carene, p-cymene, d-limonene, eucalyptol, γ-terpinene, terpinolene, linalool and α-terpineol were purchased from Aldrich (Milwaukee, WI) and Fluka (Buchs, SG, Switzerland) were used for calibration. The LODs of the target BVOCs ranged from 0.31 to 0.50 ppbv.

In addition to BVOCs, 41 VOCs were collected in a pressurized canister and measured by a GC/mass spectrometer (MS) (6890 GC/5973MS, Hewlett Packard, Palo Alto, CA) with the U.S. EPA TO-14 method (USEPA., 1999a). However, no target VOCs were detectable in the series of experiments.

3.2.2 Carbonyl sampling and analysis

Carbonyls in the air were collected into silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55-105 μm particle size, 125Å pore size; Waters Corporation, Milford, MA) with a Desert Research Institute (DRI) standard carbonyl sampler at a flow rate of 1 L min^{-1} for one hour (Ho et al., 2002). Collection efficiencies were measured under field conditions by sampling carbonyls into two identical cartridges connected in series. They were calculated as 100% $(1-A_b/A_f)$, where A_f and A_b were the amounts of a carbonyl collected on the front and the back sampling tubes respectively. No breakthrough was found at such sampling flow rates and sampling time. The flow rates were checked in the beginning and at the end of each sampling using a calibrated flow meter (Gilibrator Calibrator; Gilian Instruments, W. Caldwell, NJ). A Teflon filter assembly (Whatman, Clifton, NJ) and an ozone scrubber (Sep-Pak; Waters Corporation) were installed in front of the DNPH-silica cartridge in order to remove any particulate matters and prevent possible influence of ozone (Spaulding et al., 1999). The recovery of carbonyls collection was not affected by the ozone trap (Ho and Yu, 2002). Collocated samples were collected to examine the sample collection reproducibility, which was >95% in field. A cartridge was reserved to serve as a field blank and was handled the same way as the sample cartridges. The amounts of carbonyls detected in the cartridges were corrected for the field blank when we computed the air concentrations of the carbonyls. The DNPH-coated cartridges were stored in a refrigerator at <4 ^{o}C after sampling and before analysis.

A total of 17 carbonyls was monitored, including formaldehyde, acetaldehyde, acetone, propionaldehyde, 2-butanone (MEK), *iso*+*n*-butyraldehyde, benzaldehyde, *iso*-valeraldehyde, *n*-valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, hexanal, 2,5-dimethylbenzaldehyde, glyoxal and methyglyoxal. Unsaturated carbonyls including acrolein and crotonaldehyde were detected but their abundances were not reported in the study. The unsaturated carbonyl DNP-hydrazones can react with excess reagents to form adducts, which could not be quantified accurately due to chromatographic and response factor issues (Ho et al., 2011; Schulte-Ladbeck et al., 2001).

Each DNPH-coated cartridge was eluted with 2.0 mL of acetone-free acetonitrile (HPLC/GCMS grade, Mallinckrodt Laboratory Chemicals, Phillipsburg, NJ) to a volumetric flask. Tests have been done to demonstrate that no DNPH and its derivatives remained in the cartridge after the 2.0 mL elution. Certified calibration standards of the monocarbonyl DNP-hydrazones were purchased from Supelco (Bellefonte, PA) and diluted into concentration ranges of 0.015–3.0 mg mL^{-1}. Calibration standards of the dicarbonyls were prepared by mixing glyoxal and methylglyoxal from Sigma (St. Louis, MO) in acetonitrile with 1 mL of 100 μg mL^{-1} DNPH in an acidic aqueous solution. The mixtures were allowed to be standardised at room temperature for at least 6 hours for a complete derivatization. The final volume of each calibration mixture was made to be 2.0 mL with 8:2 (v/v) of acetonitrile/pyridine (HPLC/GCMS grade; Sigma). Concentrations of the dicarbonyl DNP-hydrazones in the calibration standards ranged from 0.01–2.0 μg mL^{-1}. Linearity was indicated by a correlation of determination (r^2) of at least 0.999. The cartridge extracts and calibration standards were analyzed by injecting 20 μL of the samples to a high-pressure liquid chromatography (HPLC) system (Series 2000, PerkinElmer, Norwalk, CT) equipped with an ultra-violet (UV) detector. The column for separation was a 4.6 x 250 mm Spheri-5 ODS 5μm C-18 reversed-phase column (PerkinElmer, Norwalk, CT) operated at room temperature. The mobile phase consisted of two solvent mixtures: mixture A, 60:30:10 (v/v) of water/ acetonitrile/tertahydrofuran; mixture B, 40:60 (v/v) of water/acetonitrile. The gradient program was 80% A/20% B for 1 minute, followed by linear gradients to 50% A/50%B for the next 8 minutes and then to 100% B for the next 10 minutes, and finally 100% C for the next 5 minutes. The flow rate was 2.0 mL min^{-1}

throughout the run. The absorbance at 360 and 420nm were used for identification of the aliphatic and aromatic carbonyls (benzaldehyde and tolualdehydes) and dicarbonyls respectively. Identification and quantification of carbonyl compounds were based on retention time and peak areas of the corresponding calibration standards. The Limit of Detection (LOD) was done by analyzing a minimum of seven replicates of a standard solution containing the analytes at a concentration of 0.02 mg mL^{-1}. It was estimated using the equation:

$$\mathrm{LOD} = t_{(\mathrm{n-1},\ 1-\alpha = 99\%)} \times S, \qquad (1)$$

where $t_{(\mathrm{n}-1,\ 1-\alpha = 99\%)}$ is the T-distribution value at n-1 degrees of freedom, and S is the standard derivation of the replicates. The LODs of the target carbonyls ranged from 0.002 to 0.010 μg mL^{-1}.The measurement precision ranged from 0.5–3.2% and 1.7-4.6% for monocarbonyls and dicarbonyls respectively.

3.2.3 Ozone and particle size distributions measurements

The ozone concentration and particle number size distributions with diameters ranging from 6 to 225 nm were monitored continuously once the floor cleaner had been dosed. Twelve of the BVOCs and seventeen of the carbonyl compounds were also quantified before and after ozone dosage. The ozone concentration was measured by a photometric ozone analyzer (Model 400E, Teledyne Instruments, San Diego, CA) and the data was recorded at a 1-minute interval. Particle size distribution of SOAs was measured by a scanning mobility particle sizer (SMPS) system with a differential mobility analyzer (Model 3080, TSI Inc.) coupled to a condensation particle counter (Model 3022, TSI Inc.).

Figure 3- 1. A large environmental chamber

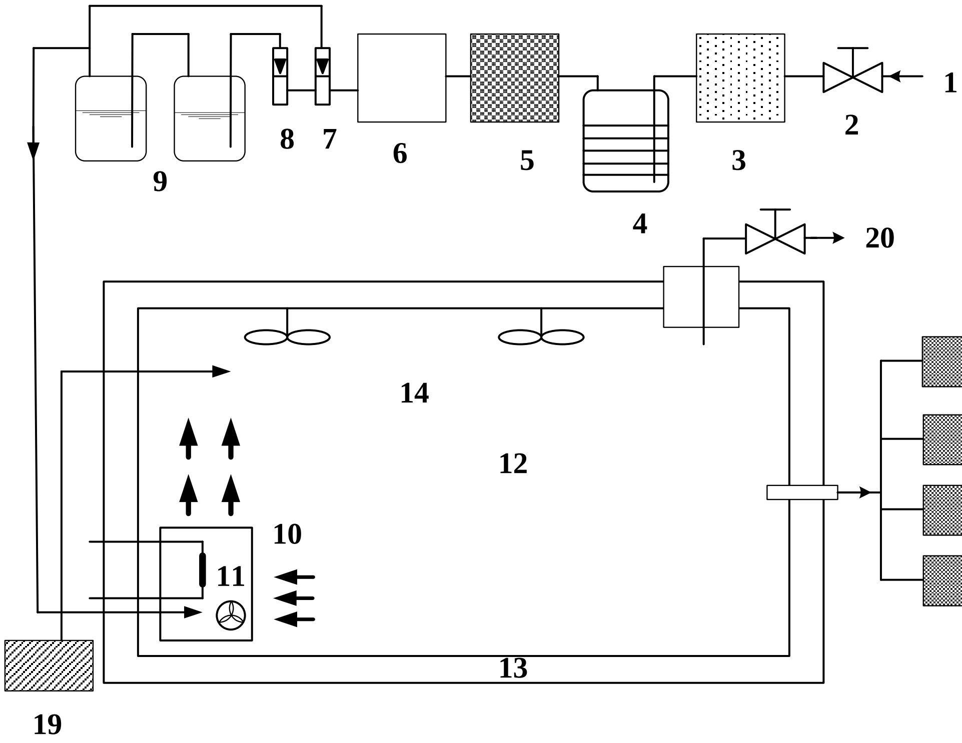


Figure 3- 2. Schematic diagram of the chamber study set-up

(1) air inlet; (2) valve; (3) blower; (4) active charcoal filters; (5) HEPA filters; (6) mass flow controllers; (7) flow controller dry air; (8) flow controller wet air; (9) humidifier; (10) rotating cylinder; (11) heating unit; (12) large environmental test chamber; (13) insulation layer; (14) mixing fan; (15) SMPS/CPC; (16) ozone monitor; (17) carbonyl sampling; (18) gas analyzer; (19) ozone generator; (20) air outlet.

Chapter 4 Development of Solid-phase Microextraction (SPME) to Determine Airborne Biogenic Volatile Organic Compounds (BVOCs) in Household Cleaning Products

4.1 Introduction

Biogenic volatile organic compounds (BVOCs), dominated by monoterpenes and oxygenated monoterpenes, are commonly used as solvents or odorants in household cleaning products which are utilized regularly in indoor environments for hygiene purposes (Destaillats et al., 2006). These unsaturated compounds are very reactive. For example, indoor BVOCs can react rapidly with ozone (O_3), producing formaldehyde, hydrogen peroxide (H_2O_2), hydroxyl radical ($\cdot OH$) and secondary ultrafine particles (D_p < 100 nm), to impose adverse effects on human health (Nazaroff and Weschler, 2004). Therefore, characterization and quantification of BVOCs either presented in or emitted from cleaning products are important to understand their roles in indoor chemistry, and an accurate and rapid measurement of BVOCs in indoor environments is crucial.

It is difficult for common analytical techniques to collect and analyze BVOCs because of their high reactivity. The traditional sampling method is to collect them onto solid adsorbents such as porous organic polymers (e.g., Tenax TA and Tenax GR) or carbon-based materials (e.g., Carbotrap and Carbograph) which are consequently thermally desorbed into a gas chromatography (GC) (Ortega and

Helmig, 2008). Analytes can be then detected using a flame ionization detector (FID) or mass spectrometer (MS). Electro-polished stainless steel canisters have also been employed in the sampling of those compounds. Whole air samples are commonly re-concentrated using cryo-focusing before being released into the GC (Pressley et al., 2004). However, the stability of these highly reactive compounds is questionable during the sampling and post-sampling period. Alternatively, solid-phase microextraction (SPME), which is a solvent-free sample collection technique that integrates sampling, isolation and concentration of the target analytes, has attracted more and more attention recently. The sampled SPME can be directly desorbed in the injection port of the GC/MS system. It usually complies with thermal desorption (TD) followed by gas chromatographic separation and various detections, and is intensively an alternative passive sampling method for environmental monitoring (Adam et al., 2005; Bouvier-Brown et al., 2007; Nicolle et al., 2008; Zeng et al., 2008), pharmaceutical (Camarasu et al., 2006) and food (Lambropoulou and Albanis, 2003) analyses. TD offers high desorption efficiency and avoids unnecessary sample dilution, leading to an increase of analytical sensitivity (Dorothea et al., 2006). SPME is suitable to be employed in indoor measurement since the air flow velocity and direction are much more stable. For instance, Larroque et al (2006) developed a SPME method for sampling representative VOCs of indoor environments including acetaldehyde, acetone, and BTX etc. The calibration curves for these compounds showed good correlation coefficients (>0.99). More recently, the emission of low molecular weight (MW) compounds from recycled high-impact polystyrene has been investigated using headspace-SPME coupled with GC/MS (Vilaplana et al.). However, equilibrium extraction processes were both adopted in these studies which required a long sampling time (normally longer than 30 minutes). This may enhance competitive adsorption and make quantification particularly challenging. In contrast, non-equilibrium short-time extraction is much preferred because it would minimize the sampling collection time and thus reduce duration variations in concentrations of target compounds. BVOCs in indoor environments, mainly from the use of household cleaning products, is a matter of increasing concern because they can react with ozone to form harmful secondary pollutants which can pose risks to human health. To the best of our knowledge, limited studies have been reported on determination of BVOCs with the SPME method in indoor environments, especially BVOCs components in household cleaning products.

In this chapter, we describe standardization of the SPME sampling, which is coupled with GC/MS detection, for quantification of airborne BVOCs. A linear correlation was shown between analytes adsorption and its mixing ratios in the atmosphere under standard environment with short-term fiber exposure. Optimal sampling parameters (i.e., sampling duration) and analytical procedures (i.e., desorption temperature and duration) were examined. The influences from air temperature (T) and relative humidity (RH) on the SPME extraction efficiency were also investigated. The feasibility of this method is demonstrated to determine the mass composition profiles of BVOCs for household floor cleaners in Hong Kong.

4.2 Study design

4.2.1 Preparation of Test Atmosphere

Liquid vaporization to a Tedlar bag was used in preparing gaseous standards for calibration and method characterization. The highest purity BVOCs standards of α-pinene, camphene, β-pinene, myrcene, 3-carene, p-cymene, d-limonene, eucalyptol, γ-terpinene, terpinolene, linalool and α-terpineol were purchased from Aldrich (Milwaukee, WI) and Fluka (Buchs, SG, Switzerland). The standards were diluted with cyclohexane (AR grade, Pestinorm, BDH, Poole, UK). A 12-L Tedlar bag (SKC Inc., Eighty Four, PA) was cleaned by filling it with air supplied by a zero air generator (Model 111, Thermo Environmental Inc., Sugar Land, TX) and evacuating it with laboratory suction at least four times before use. The clean bag was then filled with 10 L of the zero air monitored by a calibrated flow meter. A known amount of diluted standard solution was injected into the clean bag with a micro-syringe (Hamilton, Reno, NV) through a septum. Liquid vaporization was allowed by keeping the filled bag in a temperature-regulated environmental chamber at 23^{o}C for 2 hours. All discharges from the Tedlar bag were directed into a fume hood as a safety measure.

4.2.2 Solid-phase Microextraction (SPME) Method

A manual SPME sampling holder consists of a 75 μm Carboxen-PDMS fiber (Supelco, Bellefonte, PA). New fiber was heated in a GC injection port (6890 GC, Hewlett-Packard, Santa Clara, CA) at a continuous helium (He) gas flow at 300°C for 1 hour, aiming to thermally desorb any impurities. The conditioned fibers were stored properly inside a clean box in laboratory. Before sample collection, each fiber was reconditioned in the GC injection port at 300 °C for 10 minutes. Experimental results showed that no significant amount of BVOCs remained on the fiber. Each conditioned fiber was exposed in the test atmosphere for 5 minutes.

4.2.3 Sample Analysis

Once the sampling was completed, the fiber was stored and then inserted into the GC injection port at 280°C for 4 minutes. During the desorption period, the GC oven temperature was kept at 50°C. Such a temperature condition would allow the analytes released from the SPME fiber on the head of the GC column in a narrow band. The injector was kept in the splitless mode for the first 2 minutes and then switched to the split mode until the end of the GC oven temperature program. The GC oven temperature program was then started at 50 °C and was held at this temperature for 3 minutes; it was then ramped at a rate of 5°C/min to 95°C and 10°C/min to 130°C and 55 °C/min to 290 °C, and then was held at the final temperature of 290 °C for 3 minutes. A DB-5MS UI column (J&W, Agilent

Technologies, Inc., Santa Clara, CA, 30 m × 25 mm i.d. × 25 μm film thickness) was adopted for the analytes separation. The GC injector temperature was kept at 280^{o}C throughout the analysis. The carrier gas was He (ultra-high purity grade) held at a constant flow of 1.0 ml/min. The analytes after the GC separation were detected using an MS (5973 MS, Hewlett-Packard), which was operated at an ion source temperature of 230 ^{o}C and 70 eV for electron ionization (EI). The mass scan range was from 50 to 200 amu. Identification was achieved by comparing the mass spectra with NIST 08 MS library and retention time of the chromatographic peaks with that of calibration standards. The two or three most abundant ion fragments of each BVOC were selected as extract ions for the quantification. Table 4-1 summarizes the quantitative information for the target BVOCs.

4.2.4 Method Characterization

The atmosphere only with calibration solution had a RH of <1%. Test atmospheres of 18%, 30%, 50%, 80% and 90% RH were generated by injecting the amount of Milli-Q water required to achieve these RH under the same experimental conditions. The Tedlar bag was heated gently using a hair-dryer to promote the complete evaporation of the injected aliquot. In the temperature influence study, the filled bag was kept in the environmental chamber which was controlled precisely at 15, 23 and 30^{o}C (Wang et al., 2006, 2007a; Wang et al., 2007b).

4.2.5 Determination of BVOCs Compositions in Floor Cleaners

Three milliliters of each aqueous household floor cleaner was extracted with 2 ml of cyclohexane. Recovery test showed that a close to 100% of efficiency was found in the liquid-liquid extraction for BVOCs. The supernatant (cyclohexane) layer was transferred into a clean capped vial. Ten microliters of the extract was injected into the zero-air filled bag, which was also injected with Milli-Q water to adjust the RH to 18%. The air bag was conditioned in a large environmental chamber at a temperature of 23^{o}C for 2 hours. Both sample collection and analytical protocol were the same as those applied for method characterization and calibration.

Each extract was also manually injected through the GC injector at 250 ^{o}C. The injector was kept in the splitless mode for the first 2 minutes and then switched to the split mode until the end of the GC oven temperature program. The column and the MSD conditions were the same as those used in the SPME method. Calibration curves were established by plotting the peak areas of analyte versus the amounts of analytes per injection.

4.3 Results and Discussion

4.3.1 Optimization of SPME Exposure Duration

Equilibrium extraction and linear uptake are the two most popular methods employed in quantification of target air pollutants for passive sampling (Ouyang and Pawliszyn, 2007). The equilibrium extraction approach involves exposing the fibers to a sample matrix (i.e., air or water solution) until the adsorption and desorption of analytes on the fibers reach dynamic equilibrium. Once the equilibrium point was achieved, the amount of analytes adsorbed onto the fiber would not significantly increase with prolonged sampling time. However, before the dynamic equilibrium is reached, the amount of analytes adsorbed onto the fiber is linearly proportional to the amount of analytes in the sample matrix and also the fiber exposure time. Such linear uptake method is much preferred because it would minimize the sampling collection time and thus reduce duration variations in concentrations of target compounds (Bouvier-Brown et al., 2007). As a result, proper exposure time is essential to guarantee a linear correlation between the amount of analytes adsorbed onto the fiber and that contained in the sample matrix.

To evaluate threshold exposure duration, extraction efficiencies at different durations were examined by exposing the Carboxen-PDMS fibers in the Tedlar bag, which contained a mixture of the BVOCs of interest at 120 ppbv. Such concentration in the test atmosphere was higher than the emission concentrations from household cleaning products and air fresheners (Singer et al., 2006b). The threshold value is defined as the point up to which a clear linear correlation is observed by comparing the detector response to the exposure duration (in unit of minutes). Figure 4-1 demonstrates the extraction efficiency profiles for 12 BVOCs. The time required to reach the adsorption equilibrium point was much shorter for target compounds including α-pinene, camphene, β-pinene and eucalyptol, with an experimental time of 15 minutes. The duration is consistent with the value reported when a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber was used (Bouvier-Brown et al., 2007). The threshold exposure duration was 40 minutes for 3-carene. The longest threshold exposure duration was found for myrcene, p-cymene, d-limonene, γ-terpinene, terpinolene, linalool, and α-terpineol, which was longer than 120 minutes. Based on the experimental results, the extraction time of 5 minutes was selected in this study for both calibration and quantification of BVOCs in the atmospheres, minimizing any competitive adsorption onto the SPME fiber. The linear uptake of 5-minute exposure duration was further confirmed by examining the extraction efficiencies at target BVOCs concentrations of 60, 120, 1200, and 2,400 ppbv (Figure 4-2). It is important to address that the linear uptake can be affected by the amounts of other gaseous compounds that can be adsorbed by the fiber. The competition of active sites may result in prior saturation.

4.3.2 Desorption Duration

The optimal desorption duration is the minimum time that is required for complete desorption of target analytes from the SPME fiber and subsequent transfer from the GC injection port to the capillary column head. Unnecessarily longer TD time would result in peak broadening and also prolonged total analysis time (Ho and Yu, 2004). As recommended by the manufacturer, a TD temperature of $280^{o}C$ was sufficient to desorb all target BVOCs from the SPME fiber which was set to determine the optimal desorption time. Four desorption durations of 1, 2, 4, and 5 minutes were allowed to elapse before the GC temperature program started. Desorption efficiencies were accounted for by analyzing the fibers exposed in the test atmosphere under the same conditions. Figure 4-3 compares the desorption efficiencies of the target BVOCs with four different desorption durations. With the desorption duration of 1 minute, the responses of both BVOCs of interest were 20-40% lower compared with that desorbed for 4 minutes, suggesting an incomplete desorption. Lower desorption efficiencies (>20%) were also found with the desorption duration of 5 minutes. This can be attributed to the capillary column which cannot retain the BVOCs efficiently at the initial GC oven temperature of 40°C over a long desorption duration. The variation of desorption efficiencies between the desorption temperature of 2 and 4 minutes were within 10%. An optimal desorption duration of 4 minutes was thus applied to ensure the best desorption efficiency.

4.3.3 Influence from Temperature

Temperature is one of the key parameters affecting gas adsorption onto the SPME fibers. The extraction efficiencies for the target BVOCs were examined at three different temperatures of 15, 23 and 30°C with other conditions unchanged. The peak areas for the compounds sampled at 15 and 30 °C were normalized to the peak areas of corresponding compounds sampled at 23°C (Figure 4-4). In general, more analytes were adsorbed onto the SPME fiber while the temperature increased. This can be ascribed to the increase of the gas-phase molecular diffusion coefficient (denoted as D_g), which is directly proportional to temperature (Koziel et al., 2000). The increase of D_g can result in the increase of adsorbed mass under certain sampling time in turn. As reported by Koziel et al. (2000), the amount of extracted VOCs (i.e., benzene, toluene and p-xylene) mass increased almost linearly when the air temperature increased slightly from 22 to 25°C (Koziel et al., 2000). However, we did not have a similar finding for α-pinene, camphene, β-pinene and eucalyptol. The variations of extraction efficiencies were not significant over the tested temperature ranges, referring to the relatively lower boiling point of these compounds and their associated weak affinity to the fiber. Another exceptional case was for α-terpineol of which the extraction efficiency decreased at both 15 and 30 °C. This was possibly due to the reduction of adsorbent effectiveness to that compound at incongruous temperatures. The extraction efficiencies for p-cymene and linalool decreased at 15°C but were consistent at 30°C, compared with that at 23 °C. This further suggests that the fiber may operate more efficiently in adsorption of particular compounds at higher temperatures. A medium temperature of 23°C was selected as a standard for collecting both calibration standards and samples.

4.3.4 Influence from Relative Humidity

The extraction efficiencies for the target BVOCs sampled at five different RH of 18, 30, 50, 80 and 90% are shown in Figure 4-5. The presence of water vapor offered a negative effect to analyte adsorption with SPME fiber, namely, less mass was adsorbed at higher RH levels (Koziel et al., 2000). Koziel et al. (2000) demonstrated a substantial drop in mass absorption for benzene at the RH of 75%. It should be noted that the RH effect on the extraction efficiencies was ignorable for a few BVOCs of interest (e.g., α-pinene, camphene, and β-pinene). For the other compounds, the extraction efficiencies decreased generally at the RH of 30% but did not vary at the RH of 90%, compared with those at the RH of 18%. There is no specific explanation for such a phenomenon, but the results can prove that the active sites on the fiber would not be saturated by water molecules during the short extraction duration. In order to provide a consistent working environment for SPME, the RH in the sampled atmospheres was adjusted to 18%.

4.3.5 Sample Stability

Figure 4-6 compares the detector responses for the fibers being analyzed immediately and stored at 23^{o}C for 12 hours after exposure in the same test atmosphere. The variations for most target compounds were within ±10%, except linalool (16.0%), 3-carene (21.6%), γ-terpinene (30.3%) and terpinolene (30.8%). It is reasonable that a small loss of volatile BVOCs was seen along the storage duration. However, the average response of less volatile compounds including linalool, γ-terpinene and terpinolene was even higher for the fiber being stored for 12 hours than that analyzed at once. This was possibly due to large measurement deviations which were found usually for the stored samples. Considering the SPME sampling method which would be applied in future field studies, all fibers after exposure in target atmosphere were kept in the clean box for 12 hours before desorption to the GC.

4.3.6 Calibration and Limit of Detection (LOD)

The calibration curves for the tested BVOCs were constructed by exposing the SPME fiber in a gaseous BVOC mixture of known mixing ratios for 4 minutes. The mixing ratios of individual BVOCs in the Tedlar sampling bags ranged from 10 to 120 ppbv at the T of 23 ^{o}C and RH of 18%. The calibration curves were plotted as the total peak areas of the respective quantification ions versus the mixing ratio of BVOCs in the standard atmosphere. Even though many target BVOCs are constitutional or spatial isomers, their EI mass spectra are generally distinguishable. The two or three most abundant fragment ions were selected as quantification ions for each compound. The *m/z* 93 ion is the base peak in EI mass spectra of most but not for p-cymene and eucalyptol. Table 4-1 lists the calibration slopes, intercepts, and coefficients of determination, and limit of detections (LOD) for the 12 BVOCs. The coefficients of determination are all >0.99. The values demonstrate that the SPME method is reliable for quantification of BVOCs at standard conditions.

The LOD of the method is defined as the minimum amount of a selected standard that generates the minimum distinguishable signals plus three times the standard deviation of the blank signals. No peaks were detected for the BVOCs in the blank calibration samples. Hence, we approximated the mean blank signal with the calibration line intercept and the blank signal standard deviation with the standard error for the *y* (peak area ratio) estimate (Miller and Miller, 1993). The LODs in the mixing ratio were 0.31-0.50 ppbv for the 12 BVOCs. Our values are two magnitudes better than the LODs reported by Sanchez-Palomo et al. (2005) using the SPME approach with the 65-µm PDMS/DVB fiber.

4.3.7 Method Precision

Three replicates were examined for the fibers exposed in the same test atmosphere containing the BVOC mixture at a mixing ratio of 70 ppbv. The method precision was demonstrated by calculating the relative standard deviation (RSD) of the replicates, which was reported for each compound in Table 4-1. The observed RSD ranged from 1.1 to 6.7%, indicating that the passive sampling and the analytical protocol are highly reproducible in quantification of gaseous BVOCs.

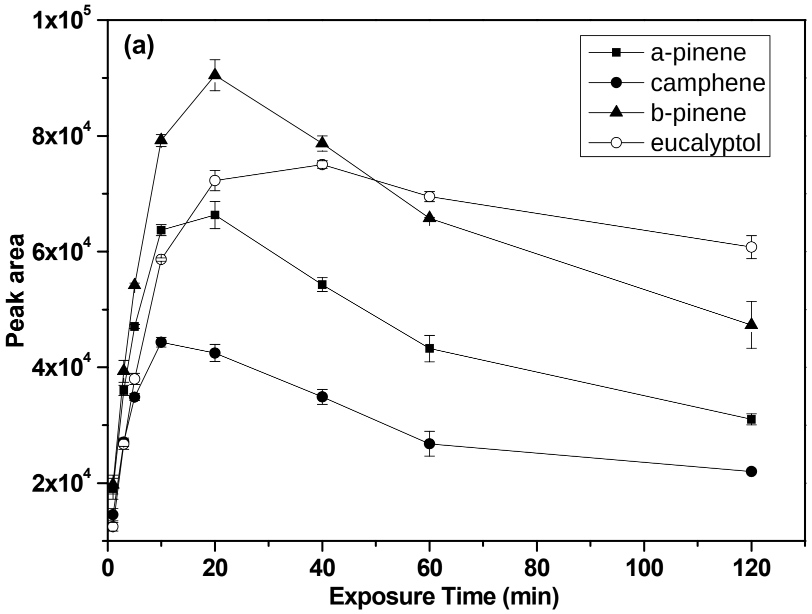
4.3.8 BVOCs Composition Profiles in Floor Cleaners

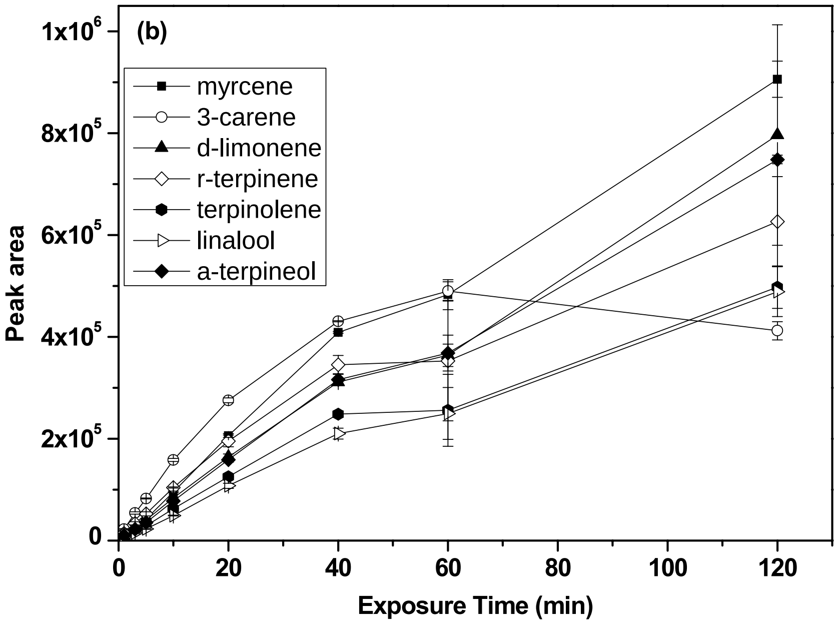
The organic extracts from four floor cleaner samples (FC#1-FC#4) were analyzed using the SPME method under optimal conditions. The samples were selected based on the extent of product consumption in Hong Kong and the scent shown on the label of their containers. The data obtained in mixing ratio was converted to mass concentration, presented in the amount of BVOC (microgram) in one gram of floor sample. Table 4-2 shows the mass concentrations for the four floor cleaner samples. The mass concentration of total quantified BVOCs for FC#1 was the highest, which was 4145 ± 888 µg per gram of the floor cleaner sample (µg/g). The total mass concentrations for other three samples were a magnitude lower than FC#1, ranging from 139 ± 3.9 to 265 ± 24.6 μg/g. Summarily, d-limonene, eucalyptol, linalool and α-terpineol were the major quantified BVOCs among the samples. β-Pinene (11.0 ± 4.5 μg/g), myrcene (215.0 ±12.1 μg/g), and p-cymene (142 ± 13.1 μg/g) were only quantifiable in FC#1. d-Limonene and linalool were the two most abundant BVOCs for FC#1, which accounted for 30.2% and 55.9% respectively, to the total quantified BVOCs. d-Limonene had a contribution of 8.9% for FC#2 and was undetectable for FC#3 and FC#4. Linalool was accounted for 35.8% and 21.3% to the total quantified BVOCs in FC#2 and FC#3 respectively. α-Terpineol was absent for FC#1 but was the most abundant BVOC for FC#2 (43.0%) and FC#3 (64.4%). Eucalyptol can be determined in both samples, accounting from 5.1 to 16.3% to the total quantified BVOCs. In addition, only two BVOCs including eucalyptol and α-terpineol were quantified in FC#4.

The amounts of BVOCs in the extract were also determined by the simple direct injection method. The extent agreement in the mass concentrations determined using the two methods could be assessed as simple linear fits. A good correlation (R^2=0.95) was found between the two methods for individual BVOCs. This demonstrates that the SPME method reports accurate and reliable data in determining airborne BVOCs under standard environments.

4.4 Chapter summary

In this chapter, the optimization of SPME method using Carboxen-PDMS fiber to quantify BVOCs with short-term fiber exposure was demonstrated. On the basis of comparison results in determination of mass concentrations in the floor cleaner extracts, the BVOCs in a standard atmosphere can be quantified accurately and precisely. The SPME approach enables a simple and rapid measurement, which could be applied for quantification of BVOCs emissions from household cleaning reagents and air refreshers in indoor environments.


(a)
Peak area
Exposure Time (min)
1x10^5
8x10^4
6x10^4
4x10^4
2x10^4
0
20
40
60
80
100
120
a-pinene
camphene
b-pinene
eucalyptol


(b)
Peak area
Exposure Time (min)
1x10^6
8x10^5
6x10^5
4x10^5
2x10^5
0
20
40
60
80
100
120
myrcene
3-carene
d-limonene
r-terpinene
terpinolene
linalool
a-terpineol

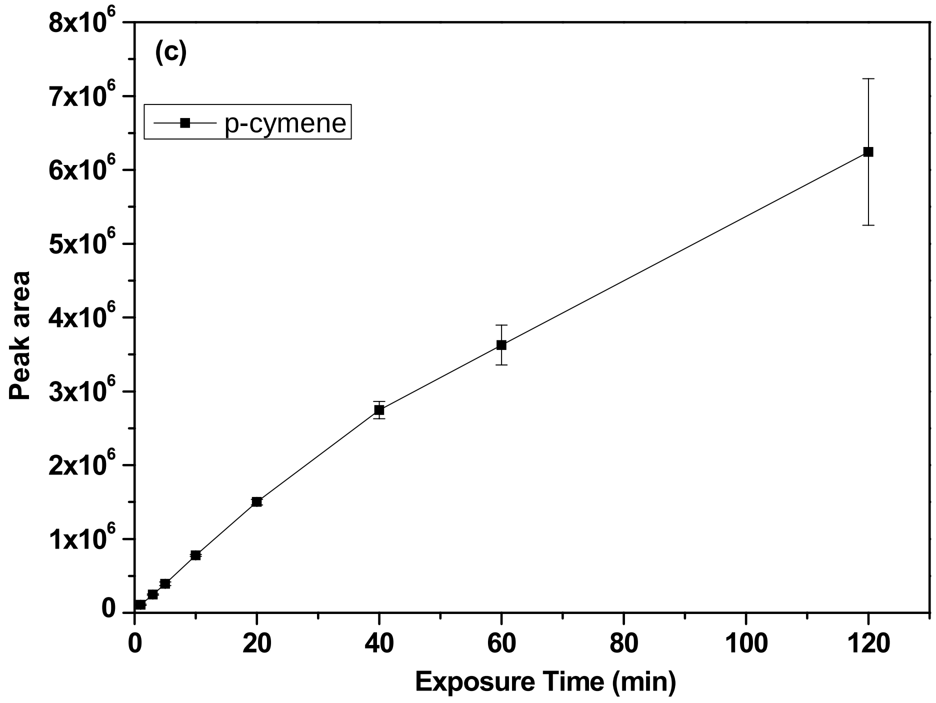
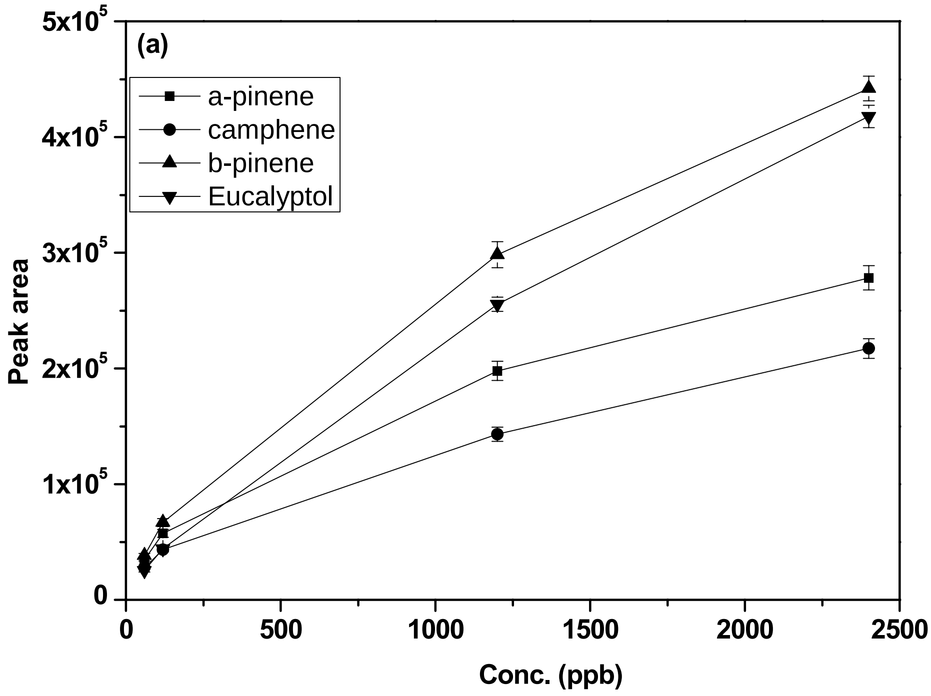
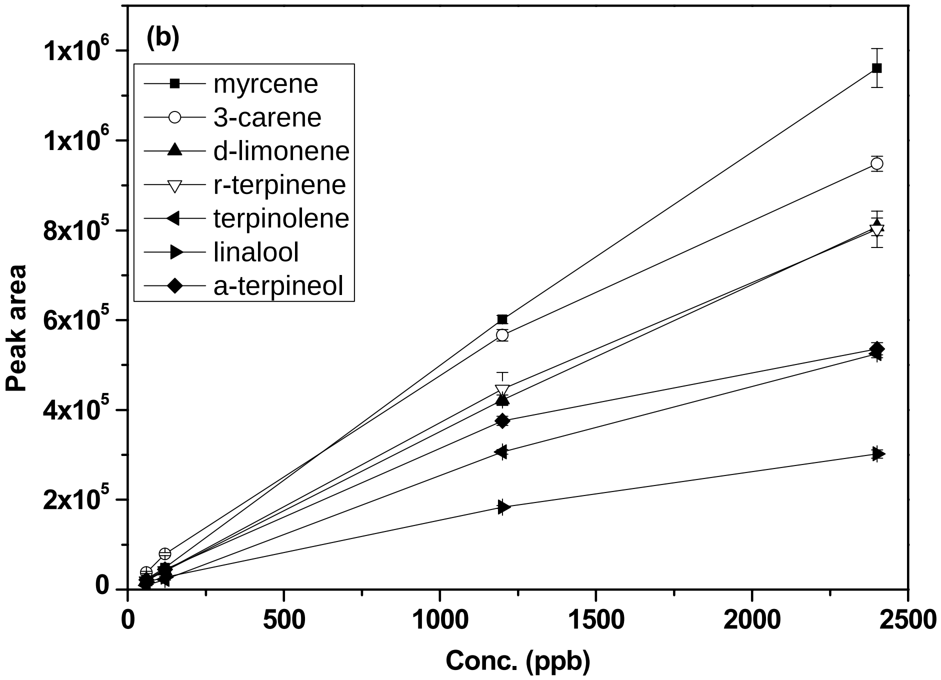


Figure 4- 1. Extraction efficiency profiles of BVOCs using the Carboxen-PDMS fiber with different exposure time. The figures were plotted as detector response (peak area) versus fiber exposure time (minutes).


(a)
a-pinene
camphene
b-pinene
Eucalyptol
Peak area
5x10^5
4x10^5
3x10^5
2x10^5
1x10^5
0
0
500
1000
1500
2000
2500
Conc. (ppb)


(b)
myrcene
3-carene
d-limonene
r-terpinene
terpinolene
linalool
a-terpineol
Peak area
1x10^6
1x10^6
8x10^5
6x10^5
4x10^5
2x10^5
0
0
500
1000
1500
2000
2500
Conc. (ppb)

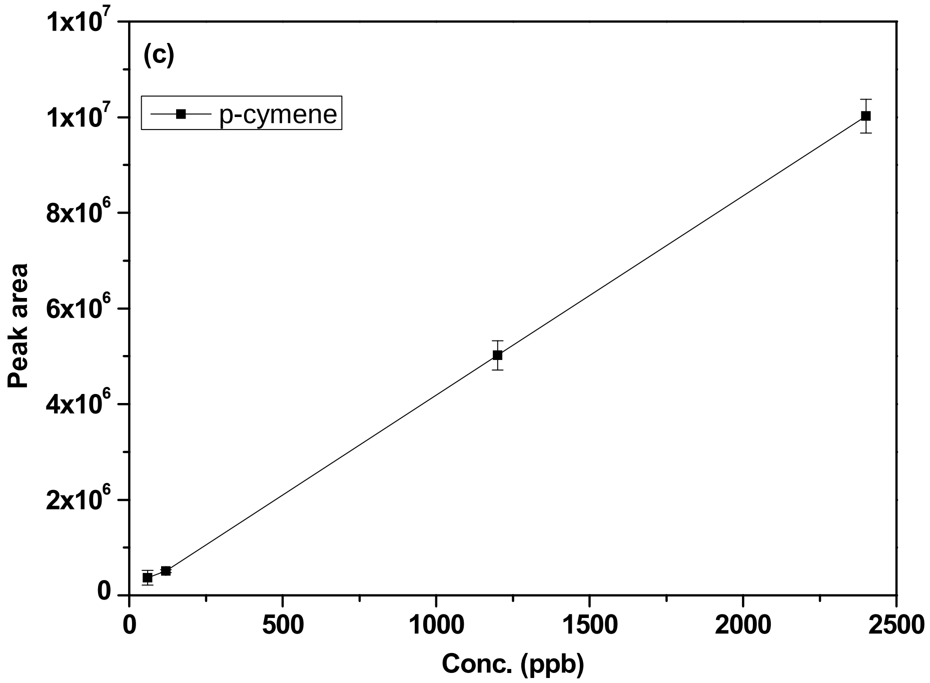


Figure 4- 2. Extraction efficiency profiles of BVOCs of different concentrations using the Carboxen-PDMS fiber with the exposure time of 5 minutes. The figures were plotted as detector response (peak area) versus the BVOCs concentration (ppbv).

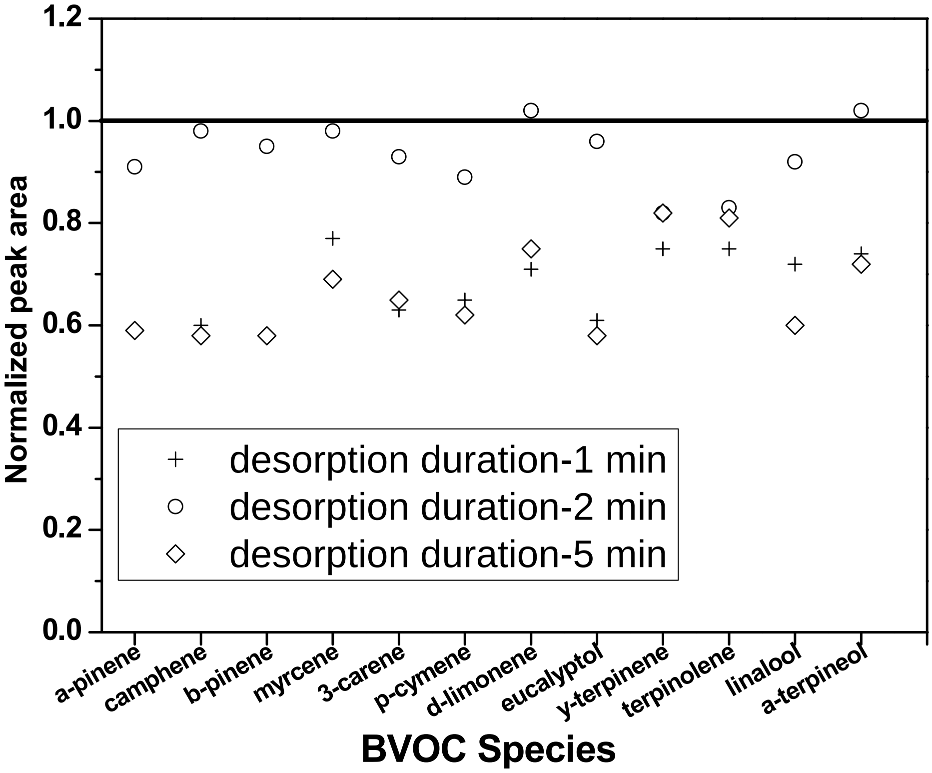


Figure 4- 3. Relative desorption efficiencies with desorption duration of 1, 2, and 5 minutes to those with 4 minutes for the target BVOCs

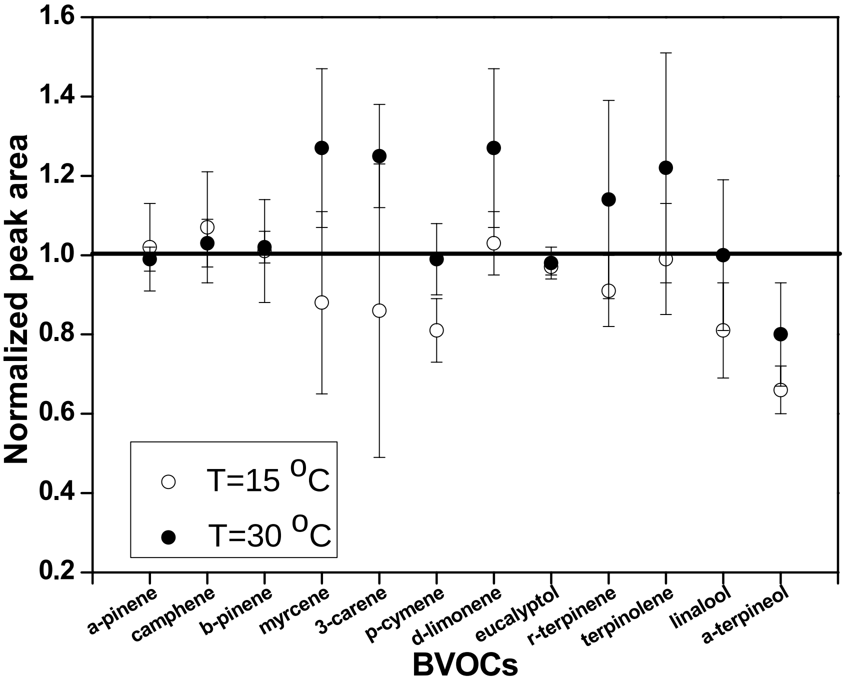


Figure 4- 4. The effect of temperature on the extraction efficiencies of BVOCs

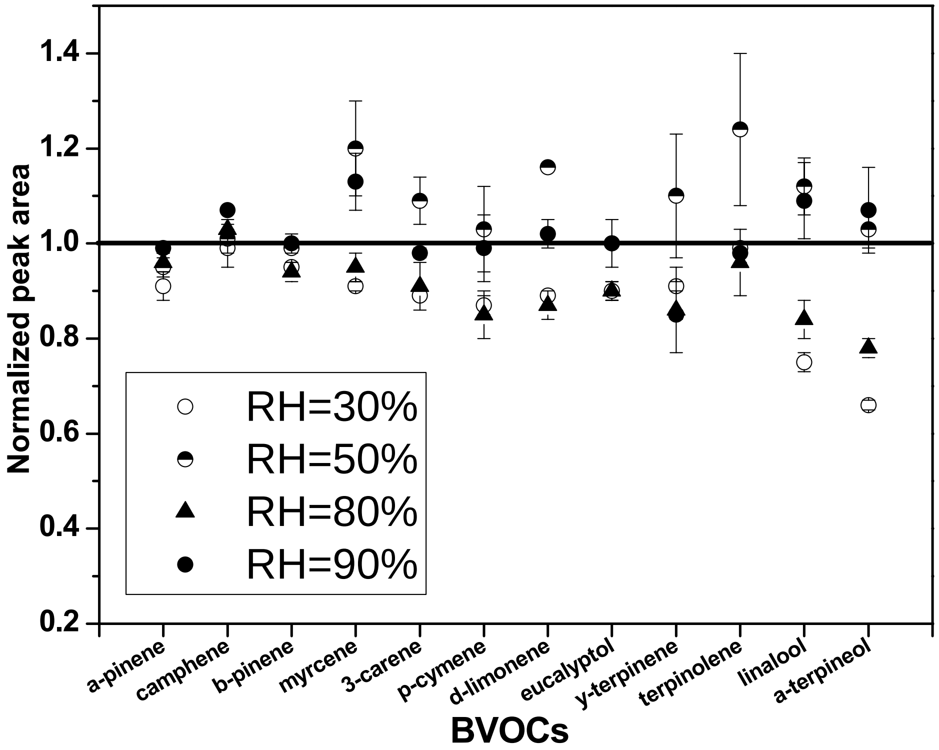
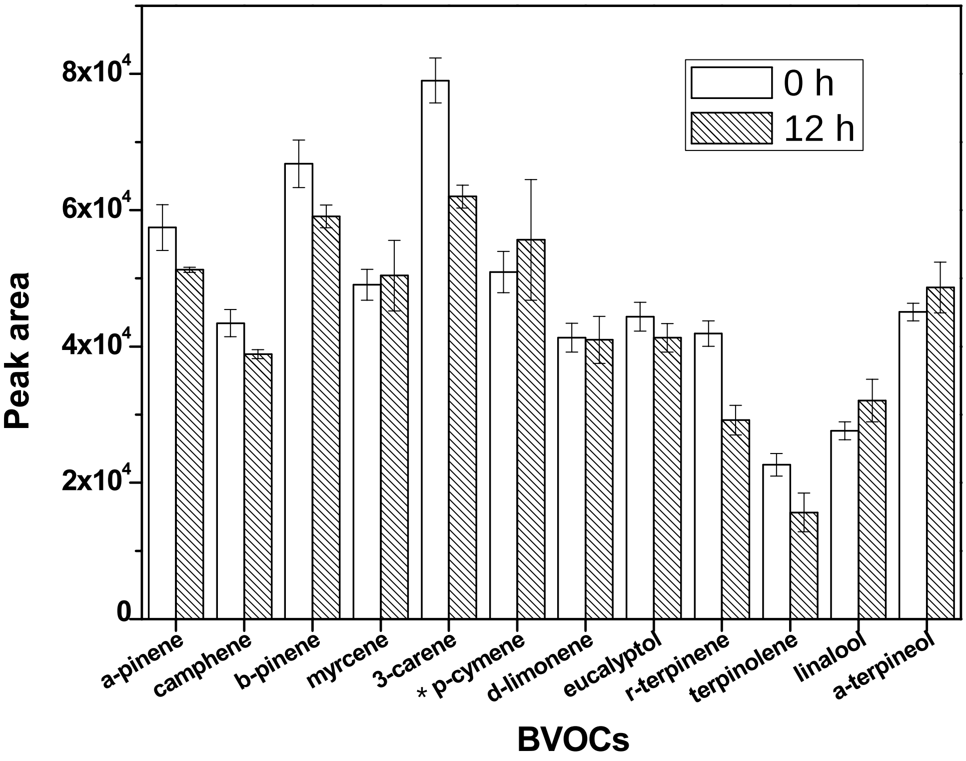


Figure 4- 5. The effect of relative humidity (RH) on the extraction efficiencies of BVOCs



*p-cymene: the detector response is divided by a factor of 10 to fix the scale for other compounds.

Figure 4- 6. Detector responses of BVOCs after collection over storage duration from 0 to 12 hours

Table 4-1. Physical Properties, Linear Regression Parameters for Calibration Curves, Limits of Detection (LODs), and Method Precisions

BVOCs	Formula	MW	Quantification Ion	Boiling Point (°C)	Slope	Intercept	R^2	LOD (ppbv)	RSD
α-Pinene	$C_{10}H_{16}$	136.23	77,93,121	155-156	286.9	105.1	0.997	0.44	1.9%
Camphene	$C_{10}H_{16}$	136.23	79,93,121	159-160	219.0	-47.8	0.999	0.48	3.3%
β-Pinene	$C_{10}H_{16}$	136.23	69,79,93	155-156	312.6	82.7	0.999	0.39	4.4%
Myrcene	$C_{10}H_{16}$	136.23	69,93	167	173.7	-22.5	0.998	0.33	5.2%
3-Carene	$C_{10}H_{16}$	136.23	77,93,121	168-169	373.5	145.4	1.000	0.45	2.3%
p-ymene	$C_{10}H_{14}$	134.22	91,119,134	176-178	1538.4	-24.2	0.994	0.50	6.7%
d-Limonene	$C_{10}H_{16}$	136.23	68,93	170-180	166.1	2.3	0.996	0.50	4.6%
Eucalyptol	$C_{10}H_{18}O$	154.25	81,108,111	176-177	199.1	-1	1.000	0.33	6.0%
γ-Terpinene	$C_{10}H_{16}$	136.23	93,119,136	182	167.3	-26.8	0.999	0.31	1.1%
Terpinolene	$C_{10}H_{16}$	136.23	93,121,136	184-185	101.9	-50.2	0.993	0.42	2.9%
Linalool	$C_{10}H_{18}O$	154.25	55,71,93	194-197	113.3	56	0.999	0.37	3.8%
α-Terpineol	$C_{10}H_{18}O$	154.25	59,93,136	217-218	199.8	-14.7	0.999	0.35	1.3%

Table 4-2. **Mass Concentrations of Targeted BVOCs in the Floor Cleaner Samples (expressed as μg of BVOC per g of floor cleaning reagent)**

Samples	β-Pinene		Myrcene		p-Cymene		d-Limonene		Eucalyptol		Linalool		α-Terpineol		Total	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
FL#1	11	4.5	215	12.1	142.2	13.1	1250	236.5	210	50.1	2317.2	571.6	nd	-	4145	888
FC#2	nd[a]	-	nd	-	nd	-	23.6	3.1	32.5	3.3	94.7	8.4	113.8	9.8	265	24.6
FC#3	nd	-	nd	-	nd	-	nd	-	20	0.7	29.7	2.1	89.6	1.1	139	3.9
FC#4	nd	-	nd	-	nd	-	nd	-	40.7	9.6	nd	-	208.6	28.1	249	37.7

[a] nd represents not detectable in sample.

Chapter 5 Characterization of Biogenic Volatile Organic Compounds (BVOCs) in Cleaning Products and Air Fresheners in Hong Kong

5.1 Introduction

Studying indoor volatile organic compounds (VOCs) is essential. Concentrations of many VOCs are higher indoors than outdoors because of particular indoor emission sources (Weisel et al., 2008). The VOCs in a domestic environment originate from a variety of sources, including utilization of consumer household products (e.g., cleaning reagents and air fresheners), emissions from adhesives, furnishing, clothing and building materials, and incense burning (Guo et al., 2000; Lee and Wang, 2004). Among the indoor VOCs, some are classified as toxic air contaminants (TACs), while a few such as formaldehyde and benzene are evidenced to be carcinogenic. Long-term exposure to the VOCs can cause adverse health effects in occupants (Guo et al., 2009).

A few studies demonstrated that daily consumptions of household cleaning reagents and air fresheners would elevate the indoor VOCs level (Singer et al., 2006b). Recently, terpenes and terpene alcohols emitted from such household products have attracted more attention because they are prone to oxidation and probably pose health risks for occupants and workers, even though such products offer substantial benefits (e.g., promotion of hygiene and aesthetics) to human life (Kwon et al., 2007b; Nazaroff and Weschler, 2004). Owing to the natural origin of terpenes and terpene alcohols, they are always classified as biogenic volatile organic compounds (BVOCs) that differentiate them from those generated by anthropogenic sources (AVOCs). Nazaroff and Weschler (2004) evidenced that household products such as floor cleaners and cleaning detergents are significant contributors for indoor air pollutants. BVOCs such as limonene, α-pinene, and myrcene have been quantified with high frequency of occurrences in the cleaning reagents sold in Korea using the headspace sampling technique (Kwon et al., 2007b). Good correlation was also found between the abundances of BVOCs in a university building and the frequency of cleaning activities, suggesting that the usage of household cleaning reagents can expose occupants to high pollutant level (Solomon et al., 2008). These BVOCs emitted from cleaning reagents and air fresheners can react rapidly with indoor ozone, resulting in the formation of secondary pollutants such as reactive radicals, airborne formaldehyde, and secondary organic aerosols (SOAs) (Coleman et al., 2008; Fan et al., 2003). The formation of SOAs has been evidenced from the ozonolysis of indoor emissions from building materials (Aoki and Tanabe, 2007), terpene-rich household products (Coleman et al., 2008), cleaning reagents and air fresheners (Destaillats et al., 2006), and wood-based materials (Toftum et al., 2008). Additionally, the products generated from oxidations of fragrance terpenes contributed greatly to fragrance allergy and upper airway irritation (Matura et al., 2005; Wolkoff et al., 2000). Such secondary formation pollutants possibly contain multiple oxygen groups that can cause adverse health effects (Forester and Wells, 2009; Jarvis et al., 2005).

In order to reduce the possible health risk on building occupants and cleaning personals, regulations to control VOC emissions from household products have been established by several governmental authorities such as United States Environmental Protection Agency (U.S.EPA), the California Air Resources Board (CARB) and the Hong Kong Environmental Protection Department (HKEPD) (CARB., 2009; HKEPD, 2007; USEPA, 1998). In order to understand the roles of BVOCs associated with the consumption of cleaning reagents and air fresheners in indoor chemistry, it is important to characterize and quantify the BVOCs composition profiles in the related products. Solid-phase microextraction (SPME) is an alternative approach for environmental monitoring that integrates sampling, isolation, and concentration for analysis with chromatographic methods (Adam et al., 2005; Bouvier-Brown et al., 2007; Nicolle et al., 2008; Zeng et al., 2008). We have demonstrated its feasibility in determination of BVOCs coupled with gas chromatography/mass spectrometric detection (SPME-GC/MS) in the previous chapter.

This chapter foucuses on evaluating the concentrations and compositions of BVOCs in cleaning products and air fresheners sold in Hong Kong and to estimate the indoor BVOCs concentrations related to the use of these products. To our best knowledge, only limited research has been carried out to quantify the mass concentrations of BVOCs in cleaning reagents and air fresheners, and none of the research has reported on local products. This study is thus critical for the establishment of regulations subject to indoor BVOCs emissions.

5.2 Experimental

5.2.1 Selection of testing samples

Four categories of household products including floor cleaners (FC), kitchen cleaners (KC), dishwashing detergents (DD), and air fresheners (AF) were examined in this study. The samples were selected based on the extent of product consumption in Hong Kong and the scent of the products shown on the label of their containers. Cleaning products consisting of lemon and pine oil were selected because they are expected to release substantial levels of reactive terpenes and related terpene alcohols. Four samples of FC, KC and DD and three samples of AF were tested and their general information is presented in Table 5-1.

5.2.2 Sample preparation

Three milliliters of each aqueous household sample were extracted with 2 mL of cyclohexane. Recovery test showed that a close to 100% of efficiency was found in the liquid-liquid extraction for BVOCs. The supernatant (cyclohexane) layer was transferred into a clean capped vial. A 12-L Tedlar bag (SKC Inc., Eighty Four, PA) was cleaned by filling it with air supplied by a zero air generator (Model 111, Thermo Environmental Inc., Sugar Land, TX) and evacuating it with laboratory suction at least four times before use. The clean bag was then filled with 10 L of the zero air monitored by a calibrated flow meter. Ten microliters of the extract was injected into the clean bag with a micro-syringe (Hamilton, Reno, NV) through a septum. Liquid vaporization was allowed by keeping the filled bag in a temperature-regulated environmental chamber at 23°C for 2 hours. All discharges from the Tedlar bag were directed into a fume hood as a safety measure.

5.2.3 Solid-phase Microextraction (SPME) Method

A manual SPME sampling holder consists of a 75 µm Carboxen-PDMS fiber (Supelco, Bellefonte, PA). New fiber was heated in a GC injection port (6890 GC, Hewlett-Packard, Santa Clara, CA) at a continuous helium (He) gas flow at 300°C for 1 hour, aiming to thermally desorb any impurities. The conditioned fibers were stored properly inside a clean box in laboratory. Before sample collection, each fiber was reconditioned in the GC injection port at 300 °C for 10 minutes. Experimental results showed that no significant amount of BVOCs remained on the fiber. Each conditioned fiber was exposed in the test atmosphere for 5 minutes.

5.2.4 Sample Analysis

Once the sampling was completed, the fiber was stored and then inserted into the GC injection port at 280°C for 4 minutes. During the desorption period, the GC oven temperature was kept at 50°C. Such a temperature condition would allow the analytes released from the SPME fiber on the head of the GC column in a narrow band. The injector was kept in the splitless mode for the first 2 minutes and then switched to the split mode until the end of the GC oven temperature program. The GC oven temperature program was then started at 50 °C and was held at this temperature for 3 minutes; it was then ramped at a rate of 5°C/min to 95°C and 10°C/min to 130°C and 55 °C/min to 290 °C, and was held at the final temperature of 290 °C for 3 minutes. A DB-5MS UI column (J&W, Agilent Technologies, Inc., Santa Clara, CA, 30 m × 25 mm i.d. × 25 μm film thickness) was adopted for analytes separation. The GC injector temperature was kept at 280 °C throughout the analysis. The carrier gas was He (ultra-high purity grade) held at a constant flow of 1.0 ml/min. The analytes after the GC separation were detected using an MS (5973 MS, Hewlett-Packard), which was operated at an ion source temperature of 230 °C and 70 eV for electron ionization (EI). The mass scan range was from 50 to 200 amu. Identification was achieved by comparing the mass spectra with NIST 08 MS library and retention time of the chromatographic peaks with those of calibration standards. The two or three most abundant ion fragments of each BVOC were selected as extract ions for the target BVOCs.

5.2.5 Calibrations

The highest purity BVOCs standards of α-pinene, camphene, β-pinene, myrcene, 3-carene, p-cymene, d-limonene, eucalyptol, γ-terpinene, terpinolene, linalool and α-terpineol were purchased from Aldrich (Milwaukee, WI) and Fluka (Buchs, SG, Switzerland). The standards were diluted with cyclohexane (AR grade, Pestinorm, BDH, Poole, UK). A known amount of diluted standard solution was injected into the zero-air filled bag. The air bag was conditioned in a large environmental chamber at temperature of 23°C for 2 hours. Both sample collection and analytical protocol were the same as those applied for sample determination.

The calibration curves for the tested BVOCs were constructed by exposing the SPME fiber in the gaseous BVOC mixture of known mixing ratios for 4 minutes. The mixing ratios of individual BVOCs in the Tedlar sampling bags ranged from 10 to 120 ppbv at the temperature of 23 °C and RH of 18%. The calibration curves were plotted as the total peak areas of the respective quantification ions versus the mixing ratio of BVOCs in the standard atmosphere. Even though many target BVOCs are constitutional or spatial isomers, their EI mass spectra are generally distinguishable. The two or three most abundant fragment ions were selected as quantification ions for each compound. The *m/z* 93 ion is the base peak in EI mass spectra of most but not for p-cymene and eucalyptol.

The limit of detection (LOD) of the method is defined as the minimum amount of a selected standard that generates the minimum distinguishable signal plus three times the standard deviation of the blank signals. No peaks were detected for the BVOCs in the blank calibration samples. Hence, we approximated the mean blank signal with the calibration line intercept and the blank signal standard deviation with the standard error for the *y* (peak area ratio) estimate (Miller and Miller, 1993). The LODs in the mixing ratio were 0.31-0.50 ppbv for the 12 BVOCs and the observed RSD ranged from 1.1 to 6.7%.

5.3 Results and discussion

5.3.1 Chemical compositions

Table 5-2 lists the mass concentrations of BVOCs in the four categories of household products (expressed as microgram of the compound in per gram of the sample) measured with the SPME-GC/MS method. Large variations in the concentrations were reported. For FC, the highest total quantified BVOCs concentration was seen in FC#1 with a mean of 4146.0 μg/g, which was at >15 times higher than that in the other three samples, ranging from 139.2 to 264.6 μg/g. d-Limonene, eucalyptol, linalool and α-terpineol were the major quantified BVOCs in FC. Among these compounds, eucalyptol was a sole compound which can be detected in all FC samples. Its mass concentrations ranged from 20.0 ± 0.7 to 210.0 ± 50.1 μg/g. Only in FC#1, other monoterpenes such as β-pinene (11.0 ± 4.5 μg/g), myrcene (215.0 ± 12.1 μg/g), and p-cymene (142.8 ±13.1 μg/g) were quantified, while they were undetectable in the rest of the samples. Linalool and d-limonene were the two most abundant BVOCs in FC#1, which contributed 55.9% and 30.2% respectively, to the total quantified BVOCs concentration. However, the contribution of linalool was significantly small in FC#2 (35.8%) and FC#3 (21.3%) and even no linalool was found in FC#4. d-limonene only contributed 8.9% in FC#2 and none was found in FC#3 and FC#4. It should be noted that α-terpineol was the most abundant BVOC in FC#2-FC#4, contributing 43.0-83.7% to the total quantified concentration, but could not be detected in FC#1. The concentrations and compositions of monoterpenes and monoterpenoids do not indicate any relationship with the fragrance presented in the FC samples. According to the information provided by the manufacturers, none of the fragrance was added in FC#1 and FC#4 and no similarity was seen on their composition profiles. Both FC#2 and FC#3 were added with lemon and pinene scent, and the mass concentrations and contributions of BVOCs varied greatly. The results demonstrate that the fragrance should not be a major contributor to BVOCs emissions from the FC.

KC and DD are the two categories of household cleaning products which are limited for uses in kitchens or cooking places. The highest total quantified BVOCs concentration (1627.3 μg/g) was seen in KC#1, while KC#3 had the lowest of 27.8 μg/g (Table 3). d-Limonene was the most abundant BVOC in all KC samples, with the mass concentrations ranging from 19.6 ± 1.0 to 1,513.0 ± 37.1 μg/g. Its contributions ranged from 44.9% to 100% to the total quantified concentrations. A few more BVOCs including p-cymene (19.8 ± 0.5 μg/g), terpinolene (72.4 ± 0.8 μg/g), linalool (14.5 ± 0.9 μg/g), and α-terpineol (7.6 ± 0.2 μg/g) were quantified in KC#1. d-Limonene was the sole monoterpene quantified in KC#2. Eucalyptol was only detected in FC#4 with the mass concentration of 22.8 ± 4.2 μg/g. In general, higher mass concentration of d-limonene was seen for the samples containing lemon fragrance (i.e., KC#1 and KC#2). No specific fragrance was present in KC#3 and KC#4 according to the package label provided by the manufacturers.

For the category of DD, only *d*-limonene was quantified in the four testing samples. The highest mass concentration of 299.0 ± 14.4 μg/g was seen in DD#4 without any fragrance. *d*-Limonene had the lowest mass concentration of 71.8 ± 3.9 μg/g in DD#1, which contained fragrances of lemon and aloe. Our results, again, showed that there was no association between the presence of fragrance and the BVOC mass concentrations.

The mass concentrations and compositions of BVOCs were quite different along the AF samples as well. The highest total quantified BVOCs concentration of 26,880.4 μg/g was found in AF#3 which was >18 times higher than in AF#1 and AF#2. d-Limonene was the most abundant BVOC in AF#3 with a mean mass concentration of 12,980.4 ± 412.6 μg/g, contributing the highest of 48.3% to the total quantified BVOCs. However, d-limonene contributed only 7.8-36.6% in the other two samples. Linalool was the most abundant BVOC in AF#1 and AF#2, with a mean mass concentration of 627.0 ± 26.4 μg g^{-1} and 1349.2 ± 49.2 μg g^{-1} respectively, contributing 63.3-91.0% to the total quantified BVOCs. Its contribution was only 34.1% in AF#3. α-Terpineol was only seen in AF#2, with a mean of 18.7±0.6 μg/g. More BVOCs including α-pinene, β-pinene, myrcene, *p*-cymene, and γ-terpinene were found in AF#3. Both AF samples contained fragrances such as lemon and jasmine flower, but their presence did not show any obvious association with either the mass concentrations or composition profiles.

5.3.2 Comparison with literature data

The mass concentrations in the household products in Hong Kong were compared with those reported in U.S. products (Table 5-3). Our unit has been converted to microgram of BVOC per milliliter of household sample for the comparison purpose. On average, the mass concentrations of BVOCs in U.S. household products were at least one magnitude higher than those in our test samples, except myrcene and linalool. d-Limonene was the most abundant BVOC in the Hong Kong samples but it was still >30% lower than the mean values of 14.7 and 17.0 mg/mL in the U.S. cleaning products and air fresheners (Singer et al., 2006b). α-Terpineol was the most abundant BVOC in the U.S. cleaning products but none was found in air fresheners. In contrast, linalool was the most abundant BVOC in the U.S. air fresheners but was undetectable in the cleaning products. Such differentiation could not be seen in the Hong Kong samples in which both α-terpineol and linalool co-existed. It should also be noted that a wider variety of BVOCs was seen in the air-fresheners in Hong Kong, compared to only limonene and α-terpineol which were found in the U.S. products. The comparisons demonstrate large deviations in the chemical compositions of the household products manufactured in the countries.

As the majority of cosmetic products and household products are scented, exposure to fragrance chemicals is immense in the population. Even though major constituents of terpenes (e.g., 3-carene, d-limonene, α-pinene, and α-terpineol) emitted from Nordic soft woods can probably be ruled out as a cause of acute eye irritation indoors (Molhave et al., 2000), products generated from the oxidation of fragrance terpenes contributes greatly to fragrance allergy (Matura et al., 2005). Karlberg et al. (1997) also found that exposure to d-limonene containing allergenic oxidation products might result in contact sensitization and dermatitis. Table 5-3 displays the second-order rate constants for the reactions between the quantified BVOCs and hydroxyl radical (·OH) at 298 K. In contrast to the rate constants for the reactions with ozone, those for the reactions with

·OH span a relatively narrow range, approximately an order of magnitude. The reaction rate constants for terpinolene, myrcene, linalool, d-limonene and α-terpineol with ozone are in descending order. For a gas-phase reaction between ozone and any BVOC emitted from the household products, it must occur at a rate competitive with air-exchange, ventilation, or other removal processes (Nazaroff and Weschler, 2004; Weschler, 2000a). In other words, the rate constant plays an important role on the resulting products and associated adverse health impacts. Additionally, a large variety in BVOCs composition profiles may result in complex health effects because each of them possesses different paths and rates in the reactions between ozone and ·OH. A discussion on potential formation of secondary pollutants associated with the consumption of cleaning products and air fresheners is presented in the following part.

5.3.3 Estimation of indoor BVOC emissions in Hong Kong

Hong Kong is a famous densely-populated city where over 70% of the people live in a small apartment with a building area less than 70 m^2 (Li et al., 2006). Due to limited landscape, tall commercial and residential buildings are closely developed that block natural wind and lead to inefficient air exchanges from indoor to outdoor environments. Any indoor residential emission sources such as use of household chemicals would thus greatly affect the indoor air quality (IAQ) in Hong Kong. The median air exchange rate (ACH) in residences in three urban U.S. metropolitan areas was 0.71 h^{-1} (Yamamoto et al.), while that in 390 Swedish homes were <0.5 h^{-1} (Bornehag et al., 2005). Because there was no report on the residential AER in Hong Kong, an AER of 0.5 h^{-1} is thus assumed in this study. BVOCs concentrations in Hong Kong residential homes caused by the consumption of cleaning products and air fresheners were estimated. According to the assumptions made by Habib et al. (2006) and Nazaroff and Weschler (2004), the daily consumptions (R, in the unit of gram per day) of FC, KC, DD, and AF were 50, 10, 10 and 15 g/day respectively, in one household unit. We assume that there is no significant variation in the consumption rates between the countries. The daily emission amount of an individual BVOC (W_i, in the unit of microgram) from one category of household products (i) is calculated as:

$$W_i = C_i \times R_i \tag{1}$$

where C_i (in unit of μg/g) is the mean concentration of an individual BVOC component in one category of the household products as determined in this study. The daily emission amount of BVOCs from all consumed household products can thus be calculated as:

$$W = W_{FC} + W_{KC} + W_{DD} + W_{AF} \tag{2}$$

The size of the apartment is also assumed with an area of 70 m^2 and 2.8 m in height (the total volume is 196 m^3). Based on these assumptions and the mass concentrations measured from the testing samples, the corresponding daily BVOCs emissions from the consumption of cleaning products and air fresheners in a local family were estimated. As indicated in Figure 5-1, the highest BVOCs concentration in residential homes is caused by floor cleaner usage (204.0 $\mu g/m^3$), followed by air fresheners (166.4 $\mu g/m^3$), kitchen cleaners (21.9 $\mu g/m^3$) and dishwashing detergents (6.2 $\mu g/m^3$). The ratio of BVOCs amount caused by the consumption of floor cleaners to the total amount caused by the usage of these four categories of household products accounted for about 51%, followed by air fresheners (42%), kitchen cleaners (5%) and dishwashing detergents (2%). The combined product of indoor BVOC concentrations (C_i) and their reaction rates with ozone (k_i) (as shown in Table 5-3), namely $\sum C_i k_i$, was used to predict the potential on secondary pollutants formation (Destaillats et al., 2006). The product varied in the order of AF > FC > KC > DD, suggesting that the consumption of air fresheners is more likely to cause secondary pollutants formation indoors.

5.4 Chapter summary

In this chapter, the characteristics of BVOCs composition in three categories of cleaning products including floor cleaners (FC), kitchen cleaners (KC) and dishwashing detergents (DD), and also air fresheners (AF) were examined by the SPME-GC/MS method. The chemical composition and concentrations of individual BVOCs varied broadly with household products due to their different functions and scents. The consumption of floor cleaners was estimated to contribute most to total indoor BVOCs in Hong Kong. Secondary products formation potential associated with the use of household products varied in the order of AF > FC > KC > DD in the presence of ozone. The findings obtained in this study significantly enhance our understanding of indoor levels of BVOCs associated with the consumption of household products. The experimental results also assist residents in improving indoor air quality (IAQ) by means of reducing usage or choosing appropriate household cleaning products.

Table 5- 1. General information of the studied cleaning products and air fresheners

Household Products	Status	Fragrance	Origin	Main Function
Floor Cleaners (FC)				
FC 1	Liquid	- [a]	Taiwan	to clean and disinfect the floor, effective in killing germs
FC 2		Lemon	Taiwan	
FC 3		Pinene Scent	Hong Kong	
FC 4		-	Hong Kong	
Kitchen Cleaners (KC)				
KC1	Liquid	Lemon	Hong Kong	to remove stuborn dirt in kitchen
KC2		Lemon	Taiwan	
KC3		-	Taiwan	
KC4		-	Hong Kong	
Dishwashing Detergents (DD)				
DD1	Liquid	Lemon & Aloe	Hong Kong	to remove tough grease from dishes
DD2		Lemon	Hong Kong	
DD3		Lemon	Hong Kong	
DD4		-	Hong Kong	
Air Fresheners (AF)				
AF1	Liquid	Lemon	Japan	to remove dust, pollen, virus, bacteria, and odor
AF2		Jasmine Flower	China	
AF3		Jasmine Flower	Taiwan	

Note: --No fragrance was labelled on the brand of the household products

Table 5- 2. BVOCs composition of cleaning products and air fresheners (in the unit of μg BVOC/ g household products)

	α-Pinene		β-Pinene		Myrcene		p-Cymene		d-Limonene		Eucalyptol		γ-Terpinene		Terpinolene		Linalool		α-Terpineol		Total
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	
Floor Cleaners (FC)																					
FC1			11.0	4.5	215.0	12.1	142.8	13.1	1250.0	236.5	210.0	50.1					2317.2	571.6			4146.0
FC2									23.6	3.1	32.5	3.3					94.7	8.4	113.8	9.8	264.6
FC3											20.0	0.7					29.7	2.1	89.6	1.1	139.2
FC4											40.7	9.6							208.6	28.1	249.3
Kitchen Cleaners(KC)																					
KC1							19.8	0.5	1513.0	37.1					72.4	0.8	14.5	0.9	7.6	0.2	1627.3
KC2									805.6	94.9											805.6
KC3									19.6	1.0									8.3	0.5	27.8
KC4							5.6	1.1	51.4	1.8	22.8	4.2							34.6	1.1	114.3
Dishwashing Detergents (DD)																					
DD1									71.8	3.9											71.8
DD2									209.1	10.0											209.1
DD3									143.0	17.8											143.0
DD4									299.0	14.4											299.0
Air Fresheners (AF)																					
AF1									362.0	5.9							627.0	26.4			989.0
AF2									114.5	1.6							1349.2	49.2	18.7	0.6	1482.4
AF3	262.4	6.9	1377.9	30.2	997.9	40.3	1598.1	82.1	12980.4	412.6			497.5	75.3			9166.2	1309.0			26880.4

Table 5- 3. Rate constants of BVOCs with ozone and OH radical, and comparison of BVOCs compositions in cleaning products and air fresheners with literature

	Reaction with OH radicals	Reaction with Ozone	This study (mg/mL)		Singer et al., 2006[b] (mg/mL)	
	$10^{12}\times k$ (298 K) (cm^3 $molecule^{-1}$ s^{-1})	$10^{17}\times k$ (298 K) (cm^3 $molecule^{-1}$ s^{-1})	Cleaning Products	Air Fresheners	Cleaning Products	Air Fresheners
α-Pinene	52.3[a]	8.4[c]	ND	0.239	1.1	No data
β-Pinene	74.3[d]	1.5[e]	0.011	1.25	0.13	No data
Myrcene	215[f]	47 (296 K)[g]	0.21	0.91	No data	No data
p-Cymene	15.1[h]	<0.005[i]	0.007-0.14	1.45	1.9	No data
d-Limonene	164[j]	21[k]	0.019-1.2	0.035-11.81	14.7	17
Eucalyptol	11.1[l]	<0.015[m]	0.015-0.202	ND	4.1	No data
γ-Terpinene	177[n]	14[o]	ND	0.45	1.8	No data
Terpinolene	225[p]	190[q]	0.1	ND	23	No data
Linalool	159[r]	43[s]	0.20-2.22	0.61-8.34	No data	65
α-Terpineol	190[t]	30[u]	0.008-0.204	0.018	67	No data

Reference:
[a,c,d,e,f,g,j,k,n,o,p,q]: (Atkinson and Arey, 2003); [b]: (Nazaroff and Weschler, 2004); [h, l]: (Corchnoy and Atkinson, 1990); [I, m]: (Atkinson et al., 1990); [r, s]: (Wells, 2005); [t, u]: (Atkinson et al., 1995).

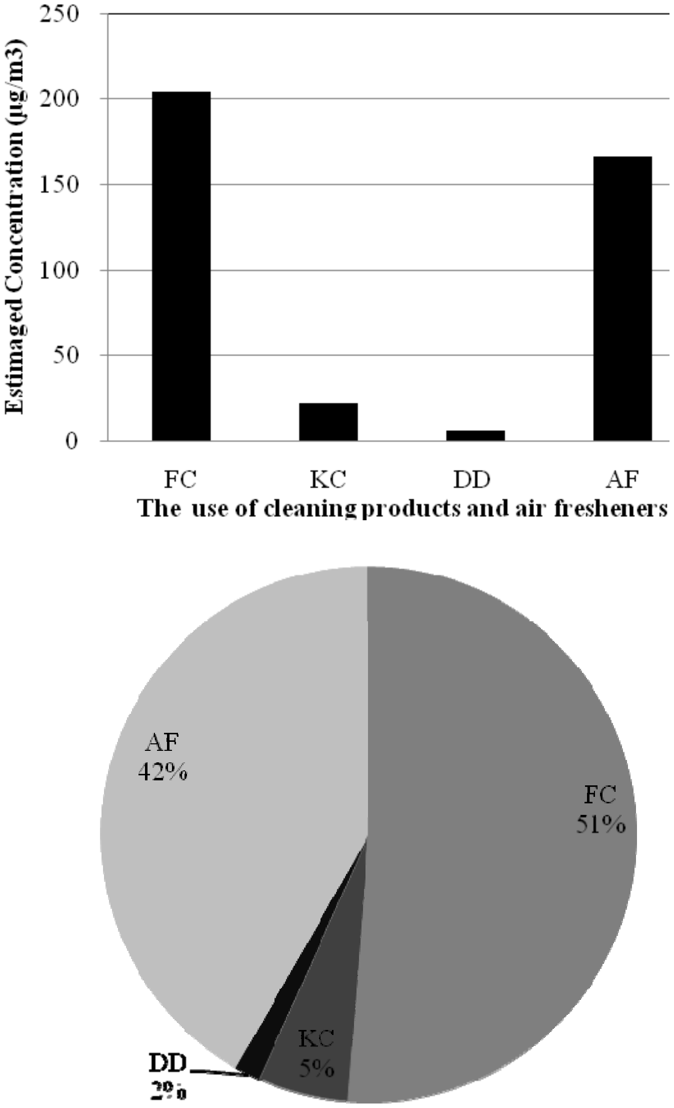


Figure 5- 1. The estimated mass concentrations (a) and fractions (b) of BVOCs caused by the consumption of cleaning products and air fresheners in residential homes in Hong Kong

Chapter 6 Physical Parameters Effect on Ozone-Initiated Formation of Indoor Secondary Organic Aerosols with Emissions from Cleaning Products

6.1 Introduction

Indoor uses of cleaning products and air fresheners lead building occupants to expose to numerous airborne chemicals (Nazaroff and Weschler, 2004). Singer et al (2006) estimated that indoor concentrations of BVOCs can reach milligram per cubic meter levels associated with cleaning products consumption, while use of air fresheners can produce tens to hundreds of micrograms per cubic meter of BVOCs(Singer et al., 2006b). A few constituents in these household products can react with pre-existing indoor oxidants (e.g. ozone) to yield potentially harmful secondary pollutants including ultrafine particles and airborne chemicals (Destaillats et al., 2006). Ozone is ubiquitous in indoor environments due to air-exchanges from outdoor air and those generated from indoor sources such as photocopiers and laser printers (Weschler, 2000b). Many studies found the “burst” growth of SOAs from reactions between indoor ozone and the BVOCs emitted from household cleaning products (Coleman et al., 2008; Destaillats et al., 2006; Lamorena et al., 2007). It is noteworthy that the surfaces of those ultrafine particles are probably nitrated or acidic (Carslaw, 2007; Carslaw et al., 2009), which can pose adverse health risks.

The formation of indoor SOAs varied under certain conditions, for example, with particular physical parameters such as air exchange rates (ACH), relative humidity (RH), and temperature (T). Diurnal or seasonal variations of these physical parameters could dramatically influence the generation and growth of indoor SOAs (von Hessberg et al., 2009). Weschler et al. (2000) found that ACH can affect indoor chemistry through altering both reaction time and initial concentrations of reactive species involved in the SOAs formations. The elevated ventilation rates not only enhance ozone infiltration from outdoors to indoors, but also boost the dilution of SOAs derived from indoor chemistry (Fadeyi et al., 2009). A few chamber studies demonstrated that T has a pronounced influence on the mass and number concentrations of SOAs generated from the reactions between BVOCs and ozone (Jonsson et al., 2008; Lamorena and Lee, 2008; Pathak et al., 2007; Saathoff et al., 2009; Svendby et al., 2008; Takekawa et al., 2003; von Hessberg et al., 2009). With the semi-empirical thermodynamic approach done by Pankow (1994; 2007) and Odum et al. (1996), the productions of SOAs increased with decreasing T because of partitioning to the condensed phase. The T can affect complicatedly on the SOAs reaction pathways, and its degree of influences varied in different environmental systems. For example, Pathak et al. (2007) showed that the yields of SOAs from the ozonolysis of α-pinene had a weak association with T between 15 and 40 ^{o}C while a much stronger T dependence was shown in the range of 0 and 15 ^{o}C. Enthalpy of precursor vaporization was found to significantly impact T dependence on the SOAs formation (Sheehan and Bowman, 2001). The amount of SOAs formed at 17^{o}C was approximately 5-6 times higher than that at 45^{o}C during the ozonolysis of α-pinene (Warren et al., 2009). RH is another critical physical parameter dramatically impacting on the SOAs formations. Jonsson et al (2008) reported that the water effect at a low T (-30 ^{o}C) could be ascribed to physical uptake and cluster stabilization, while at higher T (0 and 25 ^{o}C) the chemical reaction mechanism could also be altered (Jonsson et al., 2008).

It should be emphasized that previous studies only focused on individual BVOCs and how physical parameters influencing its reaction with ozone in a small chamber (i.e., <1 m^3 in volume). This may not fully reflect the reality for indoor environments because a mixture of different reactive BVOCs can be emitted from household cleaning products.

In this chapter, a large environmental chamber (18.26 m^3 in volume) was adopted to simulate a ventilated indoor environment. A popular floor cleaner sold in Hong Kong was selected which acted as a BVOCs emission source. The physical parameters (ACH, T, and RH) affecting the SOAs formations in the presence of ozone were investigated systematically. The ranges of these parameters are comparable to real indoor conditions in Hong Kong. Secondary reaction products of carbonyl compounds were also determined and their formation mechanism was tentatively discussed. A better understanding of those effects can assist occupants in choosing an optimal abatement method for controlling indirect generation of SOAs while the household cleaning products are being used.

6.2 Study design

6.2.1 Sample Introduction

Table 6-1 summarizes the ACH, T, RH, ozone concentration, and floor cleaner dosage in each test. The background in the chamber air was kept <10 μg m^{-3} for total volatile organic compounds (TVOCs) and < 2 μg m^{-3} for individual VOCs (Lee and Wang, 2006; USEPA., 1999b). A floor cleaner with lemon scent popularly used by Hong Kong households was selected as an emission source of BVOCs. A volume of 50 mL of the floor cleaner was transferred onto a Teflon plate (38 cm×32 cm×4 cm) which was placed on the floor in the center of the chamber. After the complete vaporization of BVOCs in the cleaning agent (3 hours), ozone was introduced into the chamber. Ozone was produced by a generator (Model 2001, Jelight Company Inc., Irvine, CA) which was fed with purified air at a pressure of 20 psi. The ozone was introduced in the chamber at a constant flow rate until a level of 45 ppbv was reached. The daily maximum 8 hours means ozone concentration is 50 ppbv as recommended by World Health Organization (WHO) in order to protect human health (Organization, 2006).

6.2.2 Sampling and analytical methods

The ozone concentration and particle number size distributions with diameters ranging from 6 to 225 nm were monitored continuously once the floor cleaner had been dosed. Twelve of the BVOCs and seventeen of the carbonyl compounds were also quantified before and after ozone dosage. The ozone concentration was measured by a photometric ozone analyzer (Model 400E, Teledyne Instruments, San Diego, CA) and the data was recorded at a 1-minute interval. Particle size distribution of SOAs was measured by a scanning mobility particle sizer (SMPS) system with a differential mobility analyzer (Model 3080, TSI Inc.) coupled to a condensation particle counter (Model 3022, TSI Inc.).

BVOCs were sampled with the solid-phase microextraction (SPME) method. A manual SPME sampling holder consists of a 75 μm Carboxen-PDMS fiber (Supelco, Bellefonte, PA). New fiber was heated in a gas chromatography (GC) injection port under continuous helium (He) gas flow at 300°C for 1 hour, aiming to thermally desorb any impurities. The conditioned fibers were stored properly inside a clean box in laboratory. Before sample collection, each fiber was re-conditioned in the GC injection port at 300 °C for 10 minutes. Experimental results showed that no BVOCs of interest remained on the fiber. For sample collection, the fiber was inserted through a sampling port and exposed for 20 minutes in the chamber. The SPME sample was once measured with a GC/flame ionization detector (FID) system (GC-17A, Shimadzu, Tokyo, Japan) by desorbing it in the injection port at 280 °C for 5 minutes. During the desorption period, the GC oven temperature was kept at 40 °C. Such a temperature condition would allow the analytes released from the SPME fiber on the head of the GC column in a narrow band. The injector was kept in the splitless mode for the first 2 minutes and then switched to the split mode until the end of the GC oven temperature program. The GC oven program was initially set at 40 °C and this temperature was held for 5 minutes; it was increased to 150 °C at a rate of 10 °C min^{-1}, then increased to 250 °C at a rate of 25 °C min^{-1}, and was finally held at such temperature for 2 minutes. A DB-5MS UI column

(30 m × 25 mm i.d. × 25 μm film thickness, J&W, Agilent Technologies, Santa Clara, CA) was adopted for the analytes separation. The flow of hydrogen and air for FID were 30 and 300 mL $\mathrm{min^{-1}}$ respectively. The detector temperature was 280 ^{o}C. Identification was achieved by comparing the retention time of the chromatographic peaks with those of calibration standards. The high purity chemical standards including α-pinene, camphene, β-pinene, myrcene, 3-carene, p-cymene, d-limonene, eucalyptol, γ-terpinene, terpinolene, linalool and α-terpineol were purchased from Aldrich (Milwaukee, WI) and Fluka (Buchs, SG, Switzerland) were used for calibration. The LODs of the target BVOCs ranged from 2 to 5 ppbv. P-cymene, d-limonene and α-terpineol were quantified from the floor cleaner with chemical compositions of 60.4±5.25, 575.0±19.0 and 135.8±36.1 μg $\mathrm{g^{-1}}$ respectively, of which d-limonene was the most abundant species accounting up to 74.6%. In addition to BVOCs, 41 VOCs were collected in a pressurized canister and measured by a GC/mass spectrometer (MS) (6890 GC/5973MS, Hewlett Packard, Palo Alto, CA) with the U.S. EPA TO-14 method (USEPA., 1999a). However, no target VOCs were detectable in the series of experiments.

6.3. Results and Discussion

6.3.1 Effect of Air Exchange Rate (ACH)

Experiments were conducted with three different ACHs of 0.36, 1.08 and 1.8 h^{-1} at constant T of 23 ^{o}C and RH of 80% (Table 6-1). The formation of SOAs was not observed with the ACH of 1.80 h^{-1} in the presence of ozone (Figure 6-1a). However, while the ACH was reduced 40% to 1.08 h^{-1}, the generation of SOAs was seen after the introduction of ozone (Figure 6-1b). Such a "burst" growth phenomenon is much obvious with the lowest testing ACH of 0.36 h^{-1} (Figure 6-1c). Figure 6-2 demonstrates the increase of the total particle number concentrations (particle diameter D_p, ranging from 6 to 225 nm) when ozone was input in the chamber with the three ACHs. The maximum particle count ($N_{6\text{-}225\ nm}$) reached 1.1×10^4 # cm^{-3} with the ACH of 0.36 h^{-1} which was one order of magnitude higher than that with the ACH of 1.08 h^{-1} (1.2×10^3 # cm^{-3}). This suggests that a higher ventilation rate can effectively dilute the BVOCs in the indoor environment, resulting in a less ultrafine particle formation in the presence of ozone. Our results agreed with the observation by Weschler and Shields (2000). Their study showed that the concentrations of indoor pollutants increased from both unimolecular and bimolecular reactions while the ventilation rate decreased. Our finding is informative for indoor environmental conservation because usual residential ACH is typically <1 h^{-1}. The average ACH was 0.71 h^{-1} at residential homes in U.S. metropolitan urban areas (Yamamoto et al., 2010) and was below 0.5 h^{-1} at Swedish homes (Bornehag et al., 2005). The average ACH is expected to be even lower than these values in high-density cities such as Hong Kong. Our observation suggests that the SOAs formation from the use of cleaning products is possibly favorable in real residential homes.

6.3.2 Effect of Temperature (T)

Figure 6-3 shows the T effects on the SOAs formation from the reaction of BVOCs and ozone with constant ACH of 0.36 h^{-1} at RH of 80%. The total particle count increased when T rose from 15 to 23 ^{o}C but then decreased at 30 ^{o}C (Figure 6-4). While the T reached 30^{o}C (Figure 6-3c), the formation of ultrafine particles was delayed in comparison with that at 15 and 23^{o}C (Figures 6-3a and b). Furthermore, the formation of ultrafine particles with D_p < 40 nm was extremely suppressed at 30^{o}C. This can be attributed to the volatilization of semi-volatile products at a high T inhibiting the nuclei formation and products condensation (Lamorena and Lee, 2008). After the ozone introduction, rapid formations of large numbers of ultrafine particles occurred, followed by particle growth. Figures 6-3a and 6-3b show uniform bimodal particle size distributions with the reaction time elapsed, reflecting the growth of particles after initial nucleation processes. When the T increased from 15 to 23 ^{o}C, the total particle number concentration ($N_{6\text{-}225\ \text{nm}}$) increased significantly from 6.32×10^3 to 1.08×10^4 # cm^{-3}. This observation was different from a few previous studies demonstrating that a lower T facilitated the formation and growth of SOAs through ozonolysis (Jonsson et al., 2008; Lamorena and Lee, 2008; Takekawa et al., 2003; von Hessberg et al., 2009) because intermediate reaction products should be more stable (Saathoff et al., 2009). In contrast, Pathak et al (2007) showed that the yields of SOAs from ozonolysis of α-pinene at atmospherically relevant concentrations had a weak dependence on T in the range of 15 and 40 ^{o}C but the influence became stronger between 0 and 15 ^{o}C (Pathak et al., 2007). Jonsson et al. (2008) also observed that the ozonolysis of limonene was the most efficient in the production of SOAs at 25 ^{o}C evidenced by both number and mass of particles formed (Jonsson et al., 2008). In our study, it is understandable that a higher T is more favorable for the evaporation and dispersion of BVOCs from liquid floor cleaner samples. However, if T is too high (e.g., >30 ^{o}C), it can inhibit the condensation of semi-volatile organic compounds (SVOCs) formed in the reactions, resulting in less SOAs generation.

6.3.3 Effect of Relative Humidity (RH)

Figure 6-5 shows the effects of RH on the formation and growth of SOAs with the constant ACH of 0.36 h^{-1} at 23 ^{o}C. When the RH was higher than 50%, the initial rate of SOA formation was higher than that at 30%. This suggests that higher RH facilitates the initial nucleation processes, which is essential for ultrafine particles formation. Additionally, a 20-minute delay of the SOA formation was observed at RH of 30%. As shown in Figure 6-6, with an increase of RH, the total particle number concentration ($N_{6\text{-}225\ nm}$) also increased obviously. The maximum total particle number concentration ($1.1\sim1.2 \times 10^4$ # cm^{-3}) was similar at the RH of 50 and 80%. The results indicate that the increases of RH can enhance the SOAs production during the ozonolysis. Jonsson et al.

(2006) found that an increase of RH from less than 2% to 85% can promote more SOAs productions from the ozone-initiated oxidation of limonene, Δ^3-carene, and α-pinene. Their later study also reported that water at a low temperature (i.e., -30 ^{o}C) could be ascribed to physical uptake and cluster stabilization, while at higher temperatures (i.e., 0 and 25 ^{o}C) the chemical mechanism or reaction rates would be altered (Jonsson et al., 2008). Tobias et al. (2000) also demonstrated that RH offers considerable influence on the chemical formations of SOAs from the reaction of 1-tetradecene and ozone (Tobias et al., 2000), suggesting that water vapor can possibly alter the chemical reaction pathways. It has recently been shown that water can alter the kinetics of radical-molecule reactions because of reduced reaction barrier heights for the complexes, thereby possibly allowing additionally energetically unfavorable reactions to take place (Vohringer-Martinez et al., 2010). We also believe that higher RH (>50%) can alter chemical reaction pathways in this study based on our experimental results. The excellent and good classes of Hong Kong indoor air quality (IAQ) objectives for offices and public places of RH are 40%-70% and 70% respectively (HKEPD, 2003). However, such a range of RH can supply favorite conditions for indoor SOA formations with the use of household cleaning products if ozone is present.

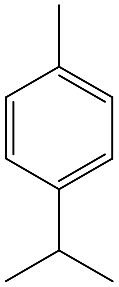
6.3.4 Formation of secondary carbonyl compounds

Figure 6-7 shows the percent yields of secondary carbonyl compounds during ozonolysis of BVOCs emitted from the floor cleaner samples. Percent yield is defined as the molar ratio of carbonyl compounds generated from the ozonolysis to the total quantified

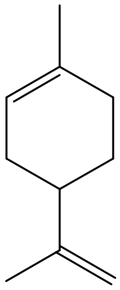
BVOCs consumed.

Acetone, followed by formaldehyde and methyl ethyl ketone (MEK), were the three most dominant carbonyls produced in the reaction. The concentrations of other monocarbonyls and dicarbonyls were below LOD. Formaldehyde and acetone are air toxics and can pose public health risks (Ho et al., 2006; Salthammer et al., 2010; WHO., 2000). Only acetone was detected which had a yield of 7.9% with the ACH of 1.80 h^{-1}. When the ACH was reduced to 1.08 h^{-1}, Formaldehyde was additionally detected. The percent yield of these two secondary carbonyls was 6.3%. MEK, in addition to formaldehyde and acetone, were detected when the ACH was further decreased to 0.36 h^{-1}. The total carbonyl yields also rose to 16.1%. Even though the particle number concentration was lower at 15^{o}C than that at 23 and 30 ^{o}C, the total carbonyl yield was the highest (i.e. 22.8%). RH had influence on the secondary carbonyl formation as well. For the RH of 30%, the yield was higher than 30%, which was the highest among the three testing RHs.

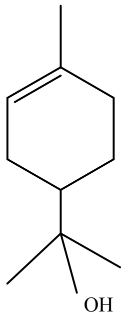
p-Cymene, d-limonene and α-terpineol were quantified in the floor cleaner sample adopted in this study with mass concentrations of 60.4±5.25, 575.0±19.0 and 135.8±36.1 μg of BVOC in one gram of floor cleaner sample (μg g^{-1}) respectively. Their molecular structures are shown as follows:



p-Cymene



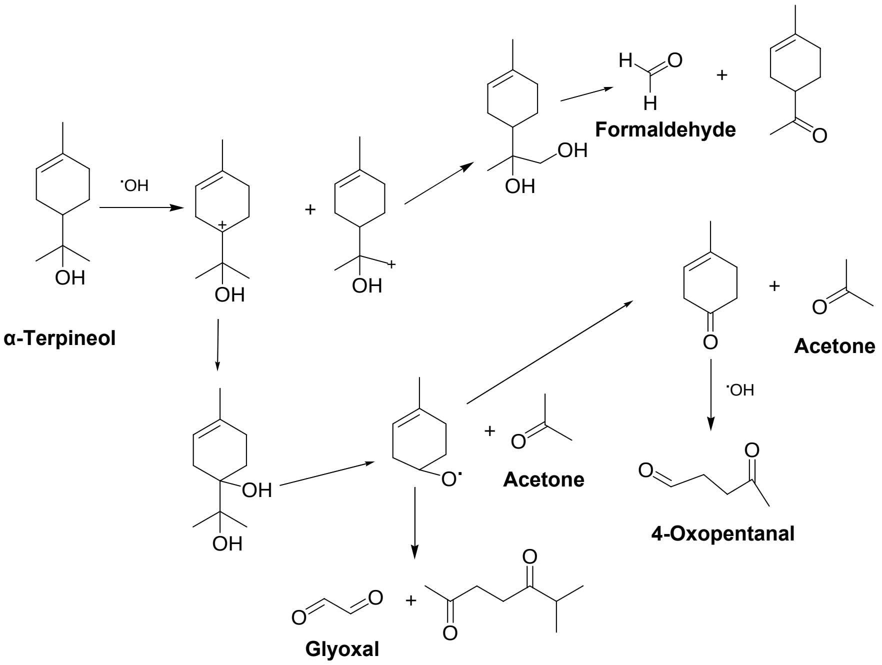
d-Limonene



a-Terpineol

Apparently, these compounds all contain at least one endocyclic double bonds, especially for d-limonene with a terminal double carbon bond. Hydroxyl radicals (·OH) can be generated from the terpene/O_3 reactions in indoor environments (Fan et al., 2003; Wells, 2005). It was shown that the yield of ·OH radical from the gas-phase reactions of O_3 with limonene was 67±10% (Aschmann et al., 2002). The concentration of ·OH strongly depends on the dynamic balance between the rate of its production and the rate of consumption by chemical reactions (Destaillats et al., 2006). The average ·OH concentration in a typical office was approximately 7×10^5 molecule cm^{-3} under natural conditions (Weschler and Shields, 1997). The generated ·OH radicals can react with BVOCs by either being added to the carbon-carbon double bond in a cyclic ring or by hydrogen abstraction.

Acetone is formed in the reaction between ·OH and α-terpineol but was not detected when ·OH scavenger (e.g., cyclohexane) of ozone is present (Forester and Wells, 2009; Wells, 2005). It was found that an increase in concentrations of acetone can be partially ascribed to the oxidation of α-terpineol by ·OH. Here concludes potential chemical pathways for the oxidation of α-terpineol by ·OH radicals to form acetone (Atkinson, 1986; Wells, 2005) :



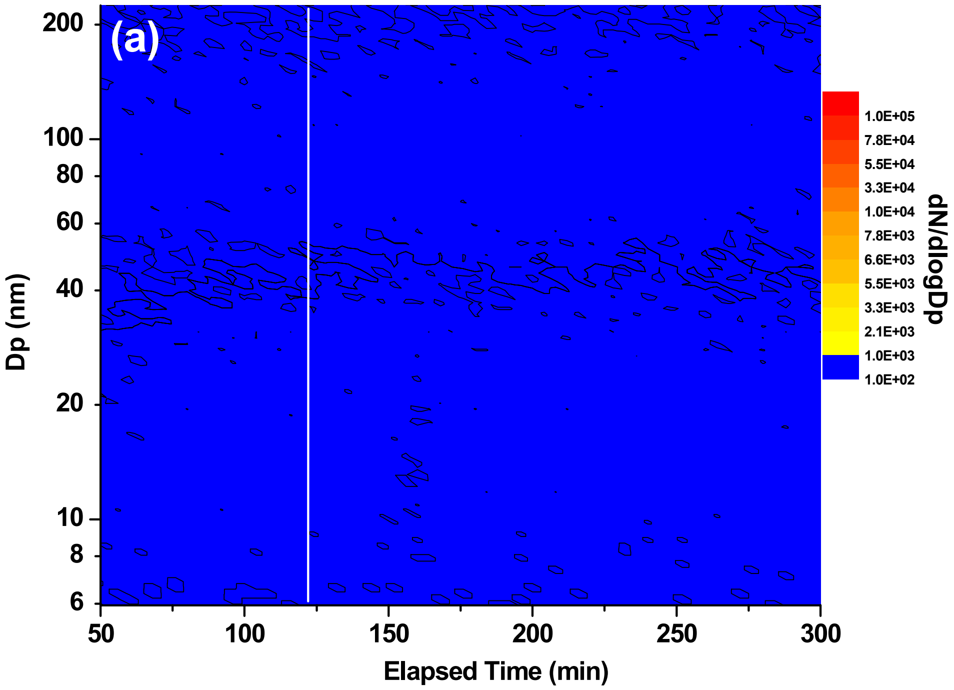
Formaldehyde, acetone, and glyoxal can be possibly generated. However, the concentrations of glyoxal were below LOD in this study, representing that its formation may be limited under our defined conditions. 4-Oxopentanol can be formed potentially but it could not be quantified with the DNPH/HPLC-UV method.

Formaldehyde can be produced as a primary carbonyl in the ozonolysis of the terminal alkenes such as d-limonene (Atkinson and Arey, 2003a). Furthermore, ·OH generated from the ozone/terpene reactions plays an important role in chemical transformations, which is responsible for approximately 56-70% of the total formaldehyde production (Fan et al., 2003). Therefore, the increase in concentrations of formaldehyde in this study could be ascribed to both the ozonolysis (primary) and ·OH oxidation reactions (secondary). Unfortunately, their contributions could not be encountered accurately without knowledge on all formation mechanisms and quantification of all potential precursors and reaction products.

Even through MEK was one of the three most important carbonyls in this study, there is a lack of information showing how it can be generated by either primary and/or secondary pathway. We assume that its production pathway should be similar to acetone owing to their similarity in chemical structures and properties of ketone. Further studies are thus needed to elucidate its role in the ozonolysis.

6.4 Chapter summary

Environmental parameters including ACH, T, and RH have significant influence on the formation and growth of SOAs from reactions between BVOC emissions from floor cleaner and ozone. With high ACH of 1.8 h^{-1}, the formation of SOA was unnoticeable after ozone dosing. However, when the ACH was reduced to 1.08 h^{-1} and 0.36 h^{-1}, the generation and growth of SOA particles was observed. High ACH can effectively dilute the BVOCs in the indoor environment, resulting in a less ultrafine particle formation in the presence of ozone. Although a higher T is more favorable for the evaporation and dispersion of BVOCs from liquid floor cleaner sample, the T may influence reversely the condensation of semi-volatile organic compounds (SVOCs) formed in the reactions if T is too high (e.g., >30 ^{o}C). Higher RH (>50%) facilitates initial nucleation processes compared with that at lower RH (30%). However, since the excellent and good classes of Hong Kong indoor air quality (IAQ) objectives for offices and public places of RH are 40%-70% and 70% respectively, it can supply favorite conditions for indoor SOA formations, leading to a hidden issue for the uses of household cleaning products if ozone is present. Acetone, followed by formaldehyde and methyl ethyl ketone (MEK), were the three most dominant carbonyls produced in the ozonolysis reaction. The carbonyl yields also varied with the physical parameters variation. The results obtained in this study are meaningful for building occupants to select proper control methods over indoor SOAs formations in real indoor environments.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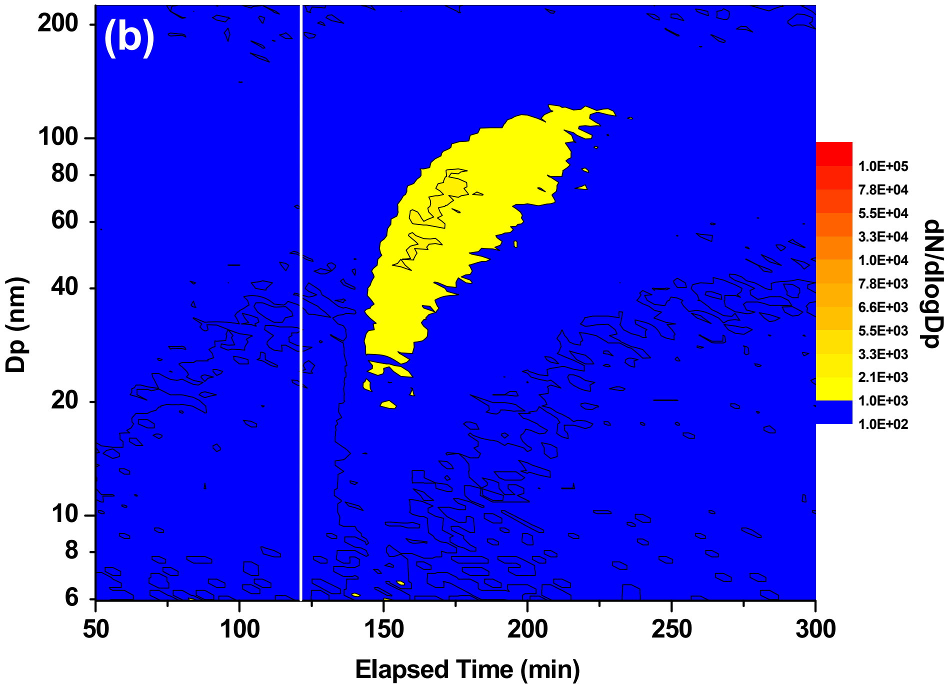
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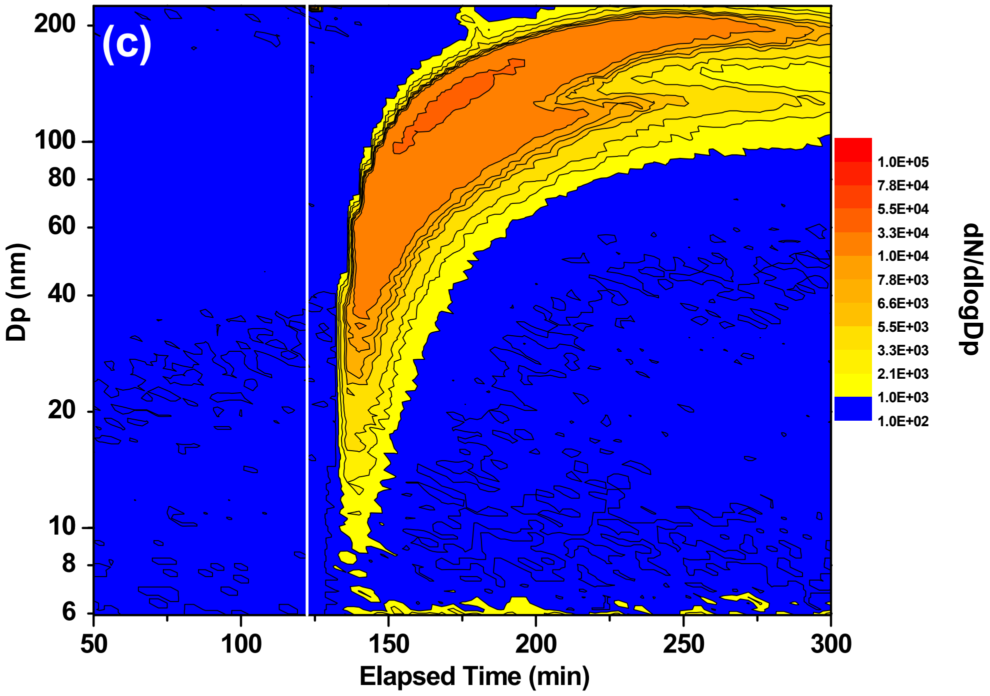


Figure 6-1. Particle size distributions of SOAs generated from the reaction between BVOCs emitted from the floor cleaner and ozone with (a) ACH=1.80 h^{-1}, (b) ACH= 1.08 h^{-1} and (c) ACH=0.36 h^{-1} at T of 23 °C and RH of 80%. The number indicated in boxes corresponds to the particle distribution dN/dlog*Dp* (# cm^{-3}) for each contour line. Ozone supply started at t=120 min and ended at t=240 min.

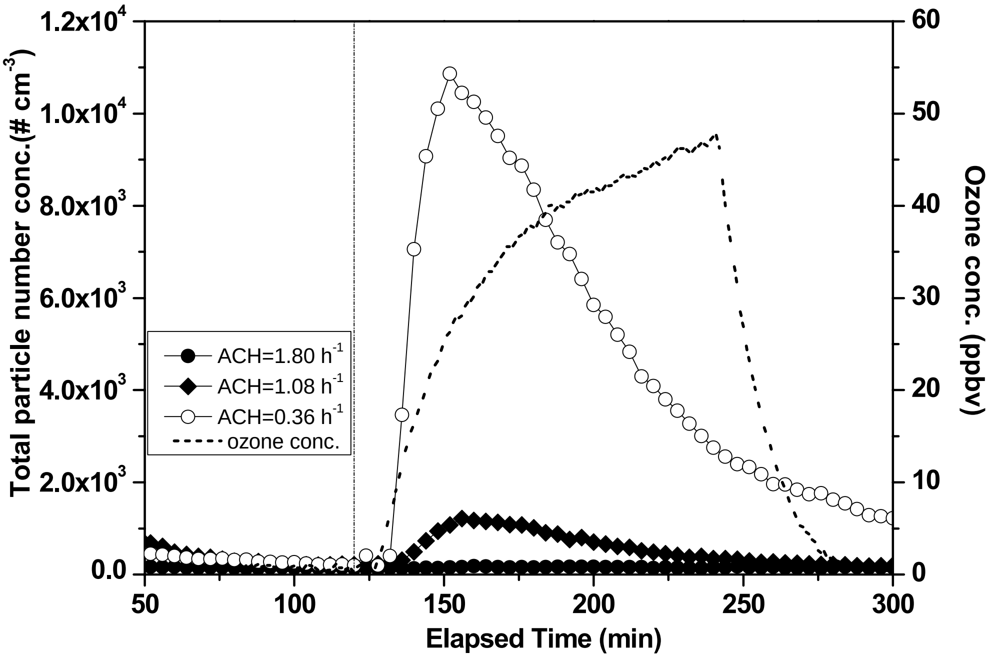
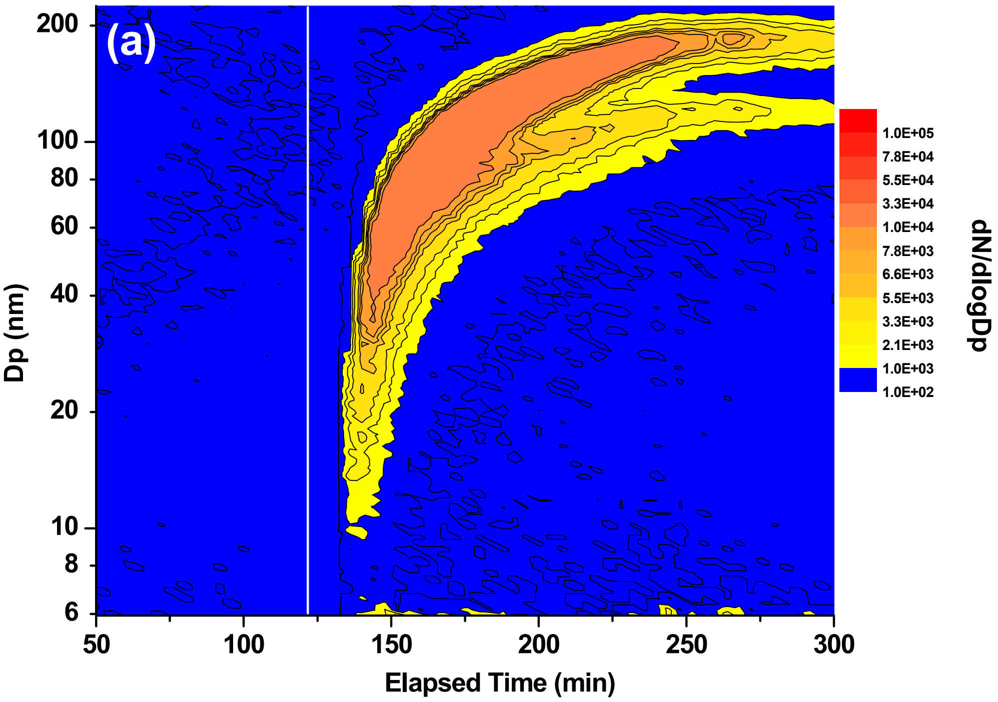


Figure 6-2. Profiles of total particle count and ozone concentration with particle diameter (Dp) ranging from 6 to 225 nm at T of 23 °C and RH of 80%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Elapsed Time (min)
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7.8E+04
5.5E+04
3.3E+04
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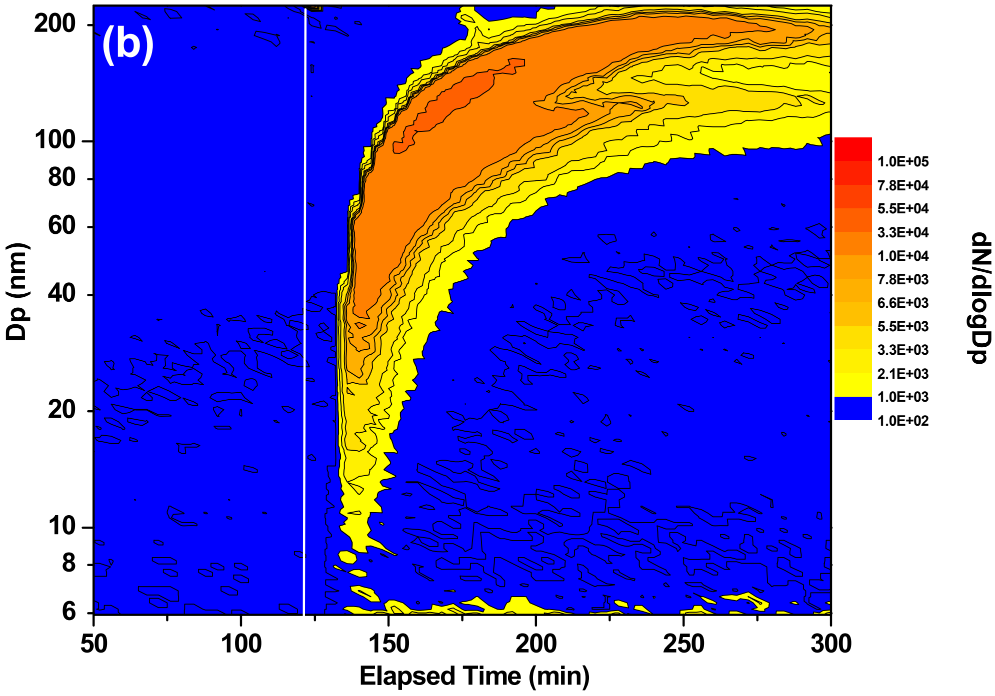
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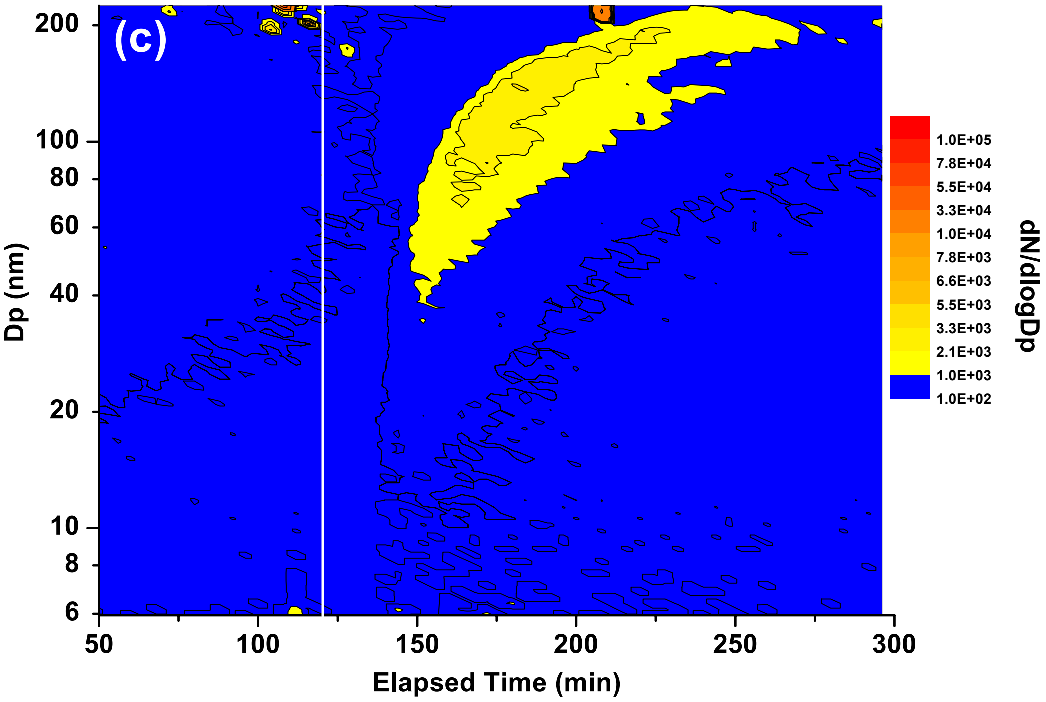


Figure 6-3. Particle size distributions of SOAs generated from the reaction between BVOCs emitted from the floor cleaner and ozone with ACH of 0.36 h^{-1} at RH of 80% and (a) T=15 °C, (b) T= 23 °C, and (c) T= 30 °C

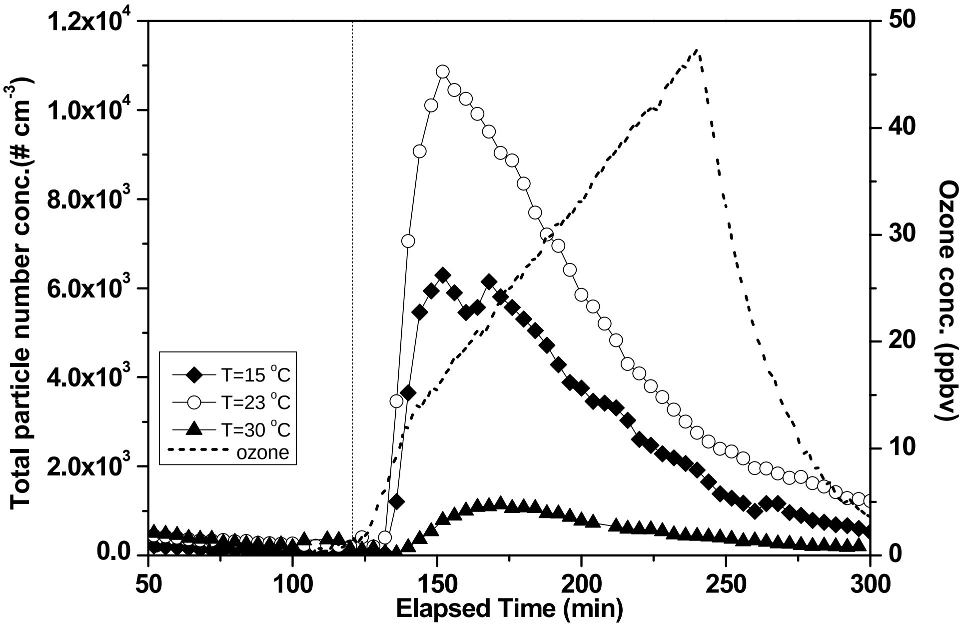
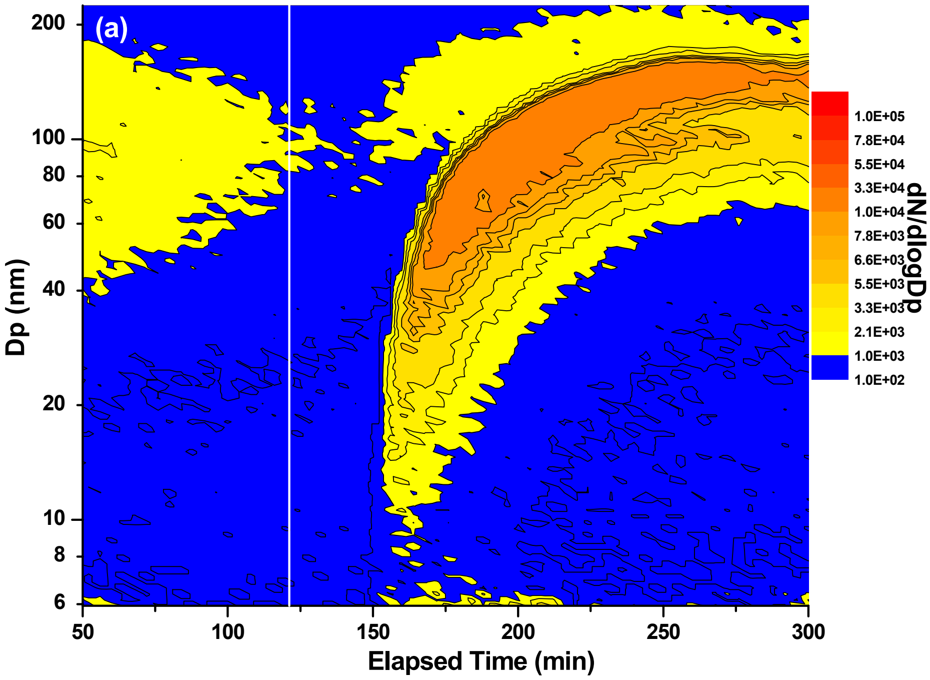


Figure 6-4. Profiles of total particle count and ozone concentration with particle diameter (Dp) ranging from 6 to 225 nm with ACH of 0.36 h^{-1}at RH of 80%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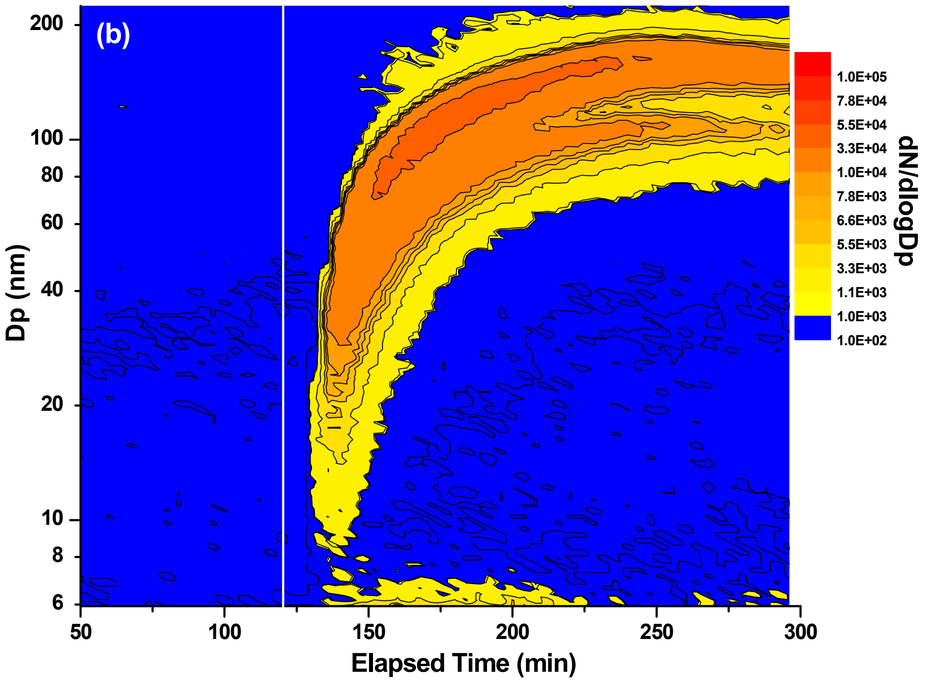
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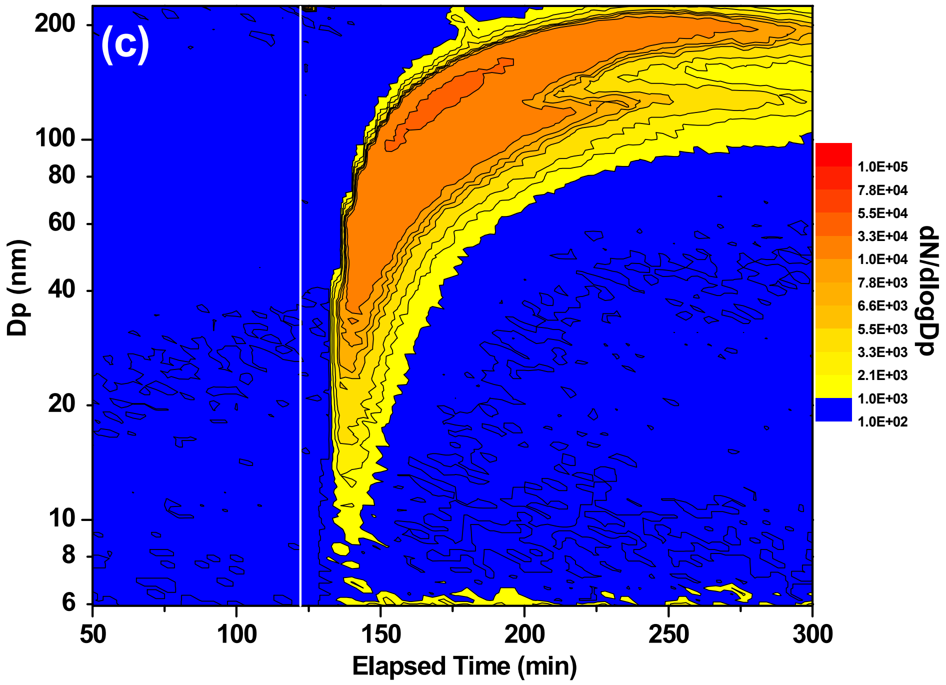


Figure 6-5. Particle size distributions of SOAs generated from the reaction between BVOCs emitted from the floor cleaner and ozone with ACH of 0.36 h^{-1} at T of 23 ^{o}C and (a) RH=30%, (b) RH=50%, and (c) RH=80%

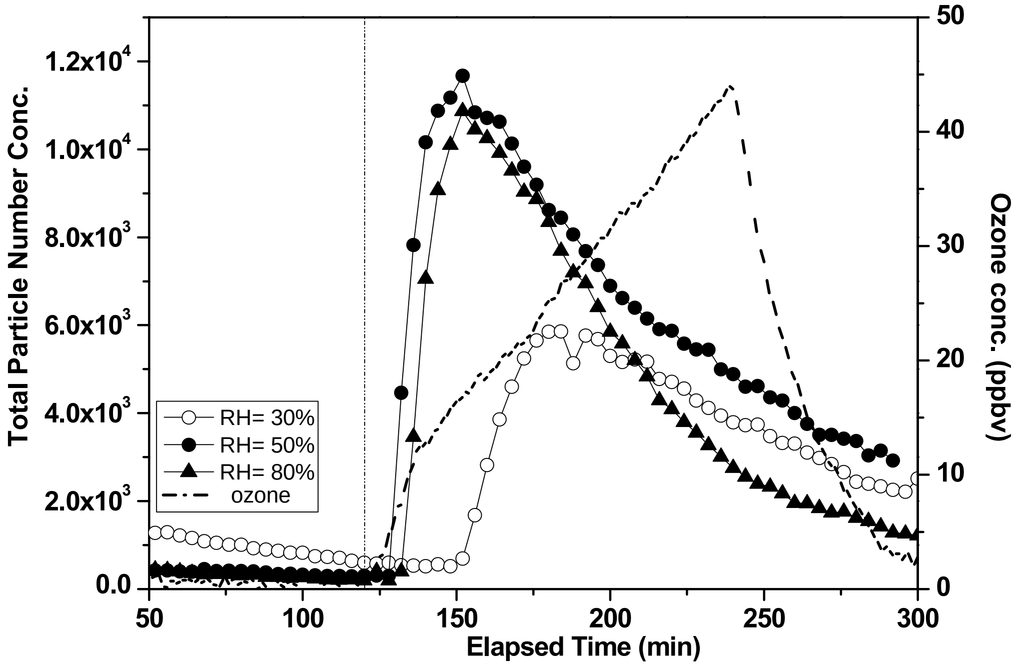


Figure 6-6. Profiles of total particle count and ozone concentration with particle diameter (Dp) ranging from 6 to 225 nm with ACH of 0.36 h^{-1}at T of 23 ^{o}C

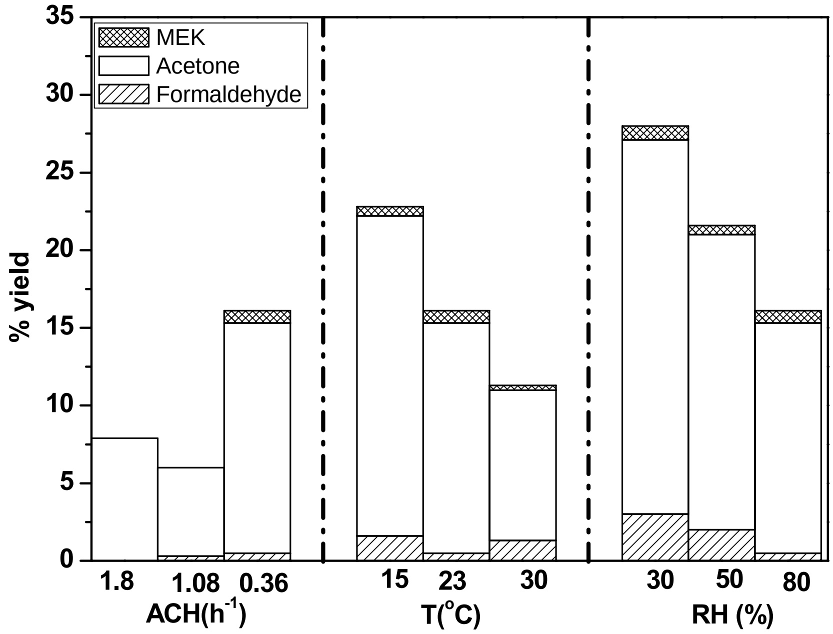


Figure 6-7. Yields of carbonyl compounds to BVOCs consumption (ppbv/ppbv)

Table 6-1. Summary of the physical parameters used to examine the reaction between BVOCs emitted from the floor cleaner and ozone in the chamber study

	Floor Cleaner Dosage (mL)	**ACH (h^{-1})**	**T (^oC)**	**RH (%)**	**Maximum Ozone Concentration (ppbv)**
ACH Effect					
	50	1.8	23	80	45
	50	1.08	23	80	45
	50	0.36	23	80	45
T Effect					
	50	0.36	30	80	45
	50	0.36	23	80	45
	50	0.36	15	80	45
RH Effect					
	50	0.36	23	80	45
	50	0.36	23	50	45
	50	0.36	23	30	45

Chapter 7 Effect of Ammonia on Ozone-Initiated Formation of Indoor Secondary Products with Emissions from Cleaning Products

7.1 Introduction

Ammonia (NH_3) is ubiquitous in ambient and indoor environments. Ambient NH_3 can be emitted by biogenic sources as well as anthropogenic sources, mainly including soil and vegetation, livestock operations, mobile exhaust, and fertilizer application (Na et al., 2007). Due to the possible health effects it causes, indoor NH_3 has attracted much more attention recently. The main indoor NH_3 source is concrete wall with addition of urea-based antifreeze admixtures (Bai et al., 2006; Tomoto et al., 2009). Gaseous NH_3 can be released from the continuous decomposition of these materials (Bai et al., 2006). NH_3 is harmful to the human body and exposure to NH_3 can cause serious symptoms such as headaches, burns, and even permanent damage to eyes and lungs (Bai et al., 2006; Lindgren; Tuomainen et al., 2003). The reported NH_3 concentration was up to 3-6 ppmv in an office (Lindgren, 2010).

The gas-phase reaction between NH_3 and inorganic acids (e.g., sulfuric acid and nitric acid) leading to significant secondary particulate formation has been well characterized (Seinfeld and Pandis, 2003), while relatively few studies have been conducted on that with organic acids indoors. Indoor chemistry dominated by ozone/terpene reactions has received most attention in the past two decades because of its substantial contribution to total human pollutant exposure (Weschler, 2004, 2011). Monoterpenes and oxygenated monoterpene species, which are the major components of biogenic volatile organic species (BVOCs), were determined at high concentration levels mainly due to the consumption of cleaning products and air fresheners indoors (Singer et al., 2006a; Singer et al., 2006b). These unsaturated BVOCs can react rapidly with ozone to form secondary pollutants, including secondary organic aerosols (SOAs), carbonyl compounds, and reactive hydroxyl radicals (Nazaroff and Weschler, 2004). The "burst" growth of SOAs which were generated from reactions between BVOCs emissions of household products and ozone in indoor environments has been observed (Coleman et al., 2008; Destaillats et al., 2006; Lamorena and Lee, 2008). It should be noted that the surfaces of these generated ultrafine particles are probably nitrated or acidic (Carslaw, 2007; Carslaw et al., 2009), which can pose adverse health risks to building occupants. Furthermore, since gaseous organic acids can be generated during BVOCs/ozone reactions, if NH_3 co-exist with these secondary products, the formation and growth of indoor aerosols should be possibly facilitated. Na et al. (2007) investigated the influence of NH_3 on SOAs formation in the α-pinene/ozone system. They found that the aerosol number and volume concentrations rapidly increased when NH_3 was added, confirming the generation of new particles from reactions between NH_3 and oxidation-generated organic acids. An opposite result was found by another study in which aerosol yields were significantly reduced after the addition of NH_3 to the styrene/ozone system. This can be probably ascribed to the rapid decomposition of intermediates (Na et al., 2006). Actually, in real indoor environments, the BVOCs are present in mixtures rather than single compounds. Forester et al. (2011) reported that the BVOCs mixtures react differently with ozone in compassion with individual components. However, little work has been conducted with respect to NH_3 effect on indoor secondary pollutants formation resulting from reactions between ozone and BVOCs emitted from household cleaning products. The potential role of ammonia chemistry on indoor secondary pollutants formation is still poorly understood.

This chapter demonstrates the effect of NH_3 on the formation of indoor SOAs and secondary carbonyls from the ozonolysis of BVOCs emitted from different categories of household cleaning products. By investigating the NH_3 effect on the ozonolysis of BVOCs mixtures in contrast to the chemistry of individual compounds, a better assessment can be made of the overall impact cleaning products posed to the real indoor environments.

7.2 Study design

All experiments were conducted in a large environmental chamber with ACH of 0.36 h^{-1}, RH of 50% and T of 23 ^{o}C.

7.2.1 Sample Introduction

Three categories of household cleaning products including floor cleaner (FC), kitchen cleaner (KC) and dishwashing cleaner (DC) which are popularly used by Hong Kong households were selected as emission sources of BVOCs. For each study, a volume of 50 mL of one category of cleaning products was transferred onto a Teflon plate (38 cm×32 cm×4 cm) which was placed on the floor in the center of the chamber. After the complete vaporization of BVOCs in the cleaning agent (3 h), ozone was introduced into the chamber. Ozone was produced by a generator (Model 2001, Jelight Company Inc., Irvine, CA) which was fed with purified air at a pressure of 20 psi. The ozone was introduced in the chamber at a constant flow rate. The daily maximum 8 h means that ozone concentration is 50 ppbv as recommended by World Health Organization (WHO) for the sake of human health (WHO., 2000). For NH_3 effect experiments, NH_3 was introduced to the chamber as soon as the cleaning products were introduced to the chamber. The NH_3 gas was supplied from a compressed gas cylinder at a concentration of 1000 ppm of NH_3 (N_2 balance, BOC gas).

7.2.2 Sampling and analytical methods

The ozone concentration and particle number size distributions with diameters ranging from 6 to 225 nm were monitored continuously once the floor cleaner had been dosed. NH_3 is measured by flowing the chamber air through a thermal oxidizer (API thermal converter, Model 501) set to 825 °C and detecting the oxidized ammonia as NO (Chemiluminescent NH_3 Analyzer-Model 201A). The thermal oxidizer is calibrated using a certified cylinder of NH_3.

Twelve of the BVOCs and seventeen of the carbonyl compounds were also quantified before and after ozone dosage. The ozone concentration was measured by a photometric ozone analyzer (Model 400E, Teledyne Instruments, San Diego, CA) and the data was record at a 1-min interval. Particle size distribution of SOAs was measured by a scanning mobility particle sizer (SMPS) system with a differential mobility analyzer (Model 3080, TSI Inc.) coupled to a condensation particle counter (Model 3022, TSI Inc.).

BVOCs were sampled with the solid-phase microextraction (SPME) method. A manual SPME sampling holder consists of a 75 μm Carboxen-PDMS fiber (Supelco, Bellefonte, PA). New fiber was heated in a gas chromatography (GC) injection port (6890 GC, Hewlett-Packard, Santa Clara, CA) under continuous helium (He) gas flow at 300^{o}C for 1 hour, aiming to thermally desorb any impurities. The conditioned fibers were stored properly inside a clean box in laboratory. Before sample collection, each fiber was reconditioned in the GC injection port at 300 °C for 10 minutes. Experimental results showed that no significant amount of BVOCs remained on the fiber. For sample collection, the fiber was inserted through a sampling port and exposed for 5 minutes in the chamber. Once the sampling was completed, the fiber was stored and then inserted into the GC injection port at 280°C for 4 minutes. During the desorption period, the GC oven temperature was kept at 50°C. Such a temperature condition would allow the analytes released from the SPME fiber on the head of the GC column in a narrow band. The injector was kept in the splitless mode for the first 2 minutes and then switched to the split mode until the end of the GC oven temperature program. The GC oven temperature program then started, which was initially set at 50 °C and was held at this temperature for 3 minutes; it was ramped at a rate of 5°C/min to 95°C and 10°C/min to 130°C and 55 °C/min to 290 °C, and was held at the final temperature of 290 °C for 3 minutes. A DB-5MS UI column (J&W, Agilent Technologies, Inc., Santa Clara, CA, 30 m × 25 mm i.d. × 25 μm film thickness) was adopted for the analytes separation. The GC injector temperature was kept at 280°C throughout the analysis. The carrier gas was He (ultra-high purity grade) held at a constant flow of 1.0 ml/min. The analytes after the GC separation were detected using an MS (5973 MS, Hewlett-Packard), which was operated at an ion source temperature of 230 °C and 70 eV for electron ionization (EI). The mass scan range was from 50 to 200 amu. Identification was achieved by comparing the mass spectra with NIST 08 MS library and retention time of the chromatographic peaks with those of calibration standards. The two or three most abundant ion fragments of each BVOC were selected as extract ions for the quantification. The high purity chemical standards including α-pinene, camphene, β-pinene, myrcene, 3-carene, p-cymene, d-limonene, eucalyptol, γ-terpinene, terpinolene, linalool and α-terpineol purchased from Aldrich (Milwaukee, WI) and Fluka (Buchs, SG, Switzerland) were used for calibration. The LODs of the target BVOCs ranged from 0.31 to 0.50 ppbv. In addition to BVOCs, 41 VOCs were collected in a pressurized canister and measured by a GC/mass spectrometer (MS) (6890 GC/5973MS, Hewlett Packard, Palo Alto, CA) with the U.S. EPA TO-14 method (USEPA., 1999a). However, no target VOCs were detectable in the series of experiments.

7.3. Results and discussion

7.3.1 NH_3 Effect on Secondary Organic Aerosols (SOAs) Formation

Figure 7-1 presents the SOAs particle size distributions from the ozonolysis of BVOCs emitted from FC in the absence and presence of NH_3. With the introduction of ozone, the "burst" growth of ultrafine particles (with D_p< 100 nm) was observed in the absence of NH_3. This finding is consistent with recent reports on the formation of SOAs from household product emissions in the presence of ozone (Destaillats et al., 2006; Singer et al., 2006a). With the coexistence of NH_3, the initial ultrafine particle formation was analogous to that in the absence of NH_3. However, particle formation was much significant in the presence of NH_3 compared with that in the absence of NH_3, especially with particle diameter ranging from 50 to 130 nm (Figure 7-1b). These nuclei mode particles accounted for the preponderance of particles by number. The maximum total particle concentration was up to 2.0×10^4 # cm^{-3} in the presence of NH_3, but was in a 35% lower of 1.3×10^4 # cm^{-3} without NH_3 (Figure 7-2a). This suggests that the new particles formation ability resulting from gas-to-particle conversion is stronger than that in the presence of NH_3. The formed particles upon ozone dosage enlarged in diameter which can be attributed to the coagulation of particles in the nuclei mode and the condensation of vapors onto existing particles (Seinfeld and Pandis, 1998). Our experimental results demonstrate that the coexistence of NH_3 pollutant has significant influence on indoor ozone chemistry, specifically ultrafine particles formation. Figure 7-2a shows the typical ozone concentration profile during the whole experimental processes. The variations of particles geometric mean diameters before and after ozone introduction with and without NH_3 presence are compared in Figure 7-2b. Before ozone introduction, the geometric mean diameters were ca 70 nm either with or without NH_3 presence. However, after ozone dosage, the geometric mean particle diameters were reduced to less than 10 nm rapidly and then enlarged to ca 110 nm. The nuclei coagulation and condensation resulted in the growth of SOAs. As shown in Figure 2b, the presence of NH_3 slightly enlarges the mean particle diameter. Particles within this size range are small enough to penetrate deeply into the human lung and have been always linked to severe short- and long-term health effects such as asthma, cardio-respiratory disease, and lung cancer (De Gouw and Jimenez, 2009).

For the household samples of KC and DD, the presence of NH_3 in the initial atmosphere had a positive relationship with particles formation (Figures 7-3 and 7-4). For KC sample, the maximum total particle concentration was up to 2.7×10^4 # cm^{-3} in the presence of NH_3, while it was only 1.4×10^4 # cm^{-3} without NH_3 existence (Figure 7-3 c). The NH_3 influence on KC sample was much stronger compared with that of FC sample. For DD sample, the maximum total particle concentration was up to 1.1×10^5 # cm^{-3} in the presence of NH_3, while it was 3.2 $\times 10^4$ # cm^{-3} without NH_3 existence (Figure 7-4 c). The NH_3 influence on DD sample was the strongest among the three categories of hosuehold cleaning products. For KC and DD samples, as shown in Figures 7-3d and 7-4d, the geometric mean particle diameters were reduced significantly in the presence of NH_3 compared with that in the absence of NH_3. This indicates that the formation rates of new ultrafine particles resulting from gas-to-particle conversions were much faster than those of particle growths.

These experimental results conclude that the extent of NH_3 effect on SOAs formation from the ozonolysis of BVOCs emissions from cleaning products is different among different cleaning products. This can be rationalized by considering the characteristics of BVOCs components in cleaning products and associated reaction byproducts with ozone. The reaction rates between ozone and different BVOCs are different. Additionally, characteristics of the reaction byproducts are expected to affect the nucleation process (Destaillats et al., 2006). As a result, different BVOCs emission components with a variety of ozone reaction constants can alter SOAs formation ability and result in the formation of different oxidation byproducts. For instance, linalool in FC sample would react with ozone that fragments its carbon backbone yielding products with fewer carbon atoms. These products are therefore less likely to nucleate or condense (Destaillats et al., 2006). Part of these oxidation-generated byproducts are organic acids that can experience gas-to-particle conversion if NH_3 is present (Na et al., 2007).

7.3.2 Effect on the Uptake of BVOCs

Figure 7-5 presents the uptake of BVOCs from FC, KC and DD in the presence of ozone with and without NH_3. Before ozone introduction, the total quantified BVOCs concentrations in the chamber atmosphere after the complete evaporation of loaded cleaning products for FC, KC and DD were 395.2±60.9 ppbv, 433.0±11.3 ppbv and 491.4±70.0 ppbv respectively. The BVOCs component fractions for the three categories of household products are shown in Figure 7-6. d-Limonene, linalool, eucalyptol, camphene and p-cymene contributed 51%, 27%, 17%, 3.7% and 1.3% respectively, to the total BVOCs for the FC sample. d-Limonene was the most abundant species in KC with a composition of 94.5%, followed by terpineolene of 3.9% and p-cymene of 1.6%. Only d-limonene was detected in the DD sample. Remarkably, d-limonene was the most abundant compound in all the three cleaning products. For the five BVOCs quantified in the FC sample, p-cymene was consumed completely under the same conditions either with or without the presence of NH_3. Camphene was consumed completely in the absence of NH_3, while the uptake percentage was 87% in the presence of NH_3. The uptake percentages of d-limonene, eucalyptol, and linalool in the absence and presence of NH_3 were 87.0 % and 91.0 %, 73.0 % and 68.0 %, and 71.0 % and 72.0 % respectively. p-Cymene, camphene and eucalyptol are relatively inert to ther other BVOCs because of their low bimolecular rate constants with ozone ($<1.5\times10^{-19}$, $<5 \times 10^{-20}$ and 9×10^{-19} cm^3 $molecule^{-1}$ s^{-1} respectively) (Atkinson et al., 1990a; Atkinson et al., 1990b). For terpineolene, linalool, and d-limonene, the reaction rate constants with ozone in descending order were 1.9×10^{-15}, 4.3×10^{-16} , and 2.1×10^{-16} cm^3 $molecule^{-1}$ s^{-1} respectively (Atkinson and Arey, 2003a; Atkinson et al., 1995). For the KC sample, the uptake percentages of p-cymene, d-limonene, and terpineolene were 37.3% and 47.1%, 57.2% and 61.3%, and 88.2% and 84.0% respectively in the absence and presence of NH_3. For DD, the uptake percentages of d-limonene were 81.1 % and 87.0 % in the absence and presence of NH_3 respectively. These results suggest that the presence of NH_3 in the reaction systems can increase the uptake of d-limonene which is the most dominant BVOC compound in the cleaning products.

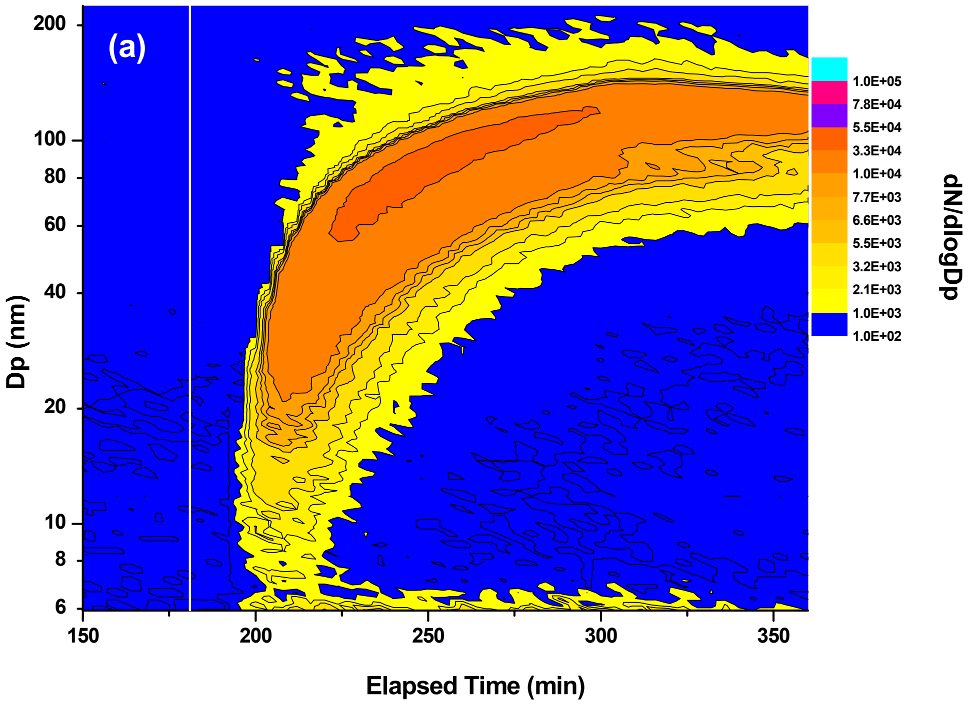
7.3.3 Effect on the Formation of Secondary Carbonyl Compounds

The percent yields (%) of secondary carbonyl compounds generated from the ozonolysis of BVOCs emitted from three categories of cleaning products were identified in the presence and absence of NH_3.The percent yields is defined as the ratio of carbonyl compounds generated to the total quantified BVOCs uptaked (ppbv/ppbv). Figure 7-7 shows the yields of carbonyl compounds from the ozonolysis of BVOCs emitted from FC, KC and DD samples in the presence and absence of NH_3. As shown in Figure 4a, acetone, followed by formaldehyde and acetaldehyde, were the three most dominant carbonyls produced in the reaction. Dicarbonyl compound, methylglyoxal, was also quantified. In the presence of NH_3, the yields of formaldehyde and acetaldehyde were slightly higher than those without NH_3. However, the yields for acetone and methylglyoxal were almost unchanged under the same conditions. For the KC and DD samples (Figure 7-7b and 7-7c), the yields of acetone were not as high as those for the FC sample under the same experimental conditions. In the presence of NH_3, acetaldehyde was below LOD (Figure 7-7b). For the DD sample, of which only d-limonene was quantified, the yields of formaldehyde and acetaldehyde were the highest among all the three categories of cleaning products. Formaldehyde can be generated as a primary carbonyl compound during ozonation of terminal alkenes such as d-limonene (Atkinson and Arey, 2003a; Destaillats et al., 2006).

According to our experimental results, the presence of NH_3 in the reaction system can significantly enhance the generation of ultrafine SOAs for all of the cleaning products. As reported by Na et al. (2007), condensable salts could be formed in the α-pinene ozonolysis system while NH_3 was present. It was commonly explained that low volatility organic acids such as pinic acid and pinonic acid would be generated during the oxidation of biogenic hydrocarbons (Kavouras et al., 1999; Yu et al., 1999). In our chamber reaction system, organic acids were also expected to be the major byproducts. These generated organic acids can react with NH_3 to form condensable salts of low volatility. This can probably contribute to the increase of SOAs particle number concentration.

7.4 Chapter summary

This laboratory investigation illustrates the potential impact of NH_3 on ozone-initiated indoor chemistry involving constituents of common household cleaning products regarding the formation of SOAs and secondary carbonyl compounds. By investigating the NH_3 effect on the ozonolysis of BVOCs mixtures in contrast to the chemistry of individual compounds, a better assessment can be made of the overall impact cleaning products have on real indoor environments.


(a)
200
100
80
60
40
20
10
8
6
Dp (nm)
150
200
250
300
350
Elapsed Time (min)
1.0E+05
7.8E+04
5.5E+04
3.3E+04
1.0E+04
7.7E+03
6.6E+03
5.5E+03
3.2E+03
2.1E+03
1.0E+03
1.0E+02
dN/dlogDp

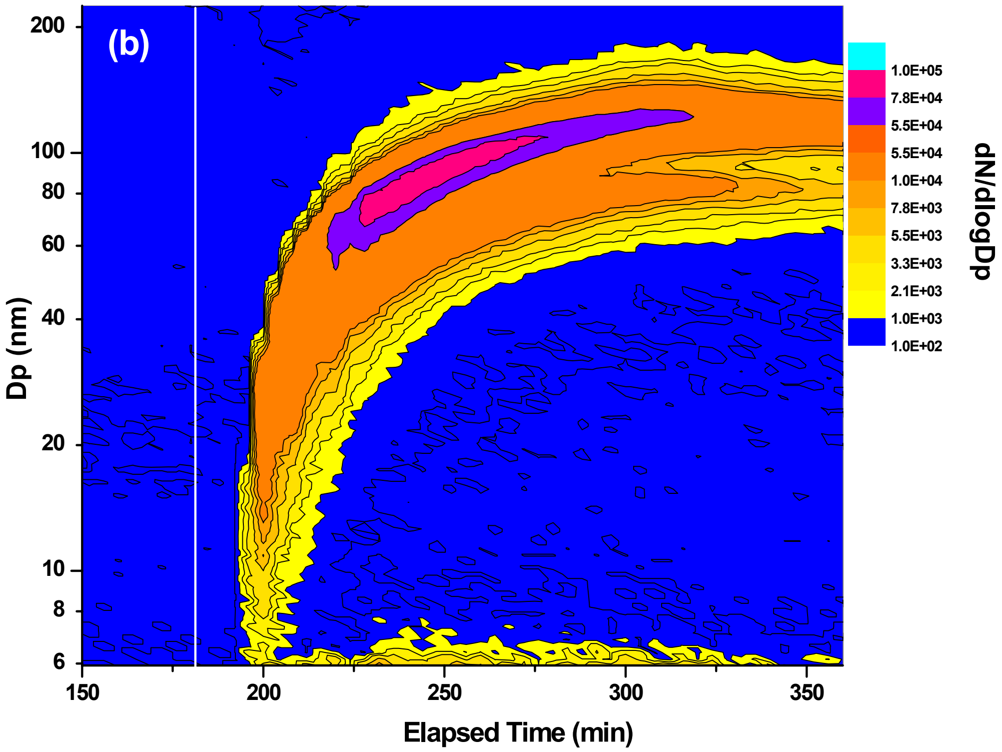
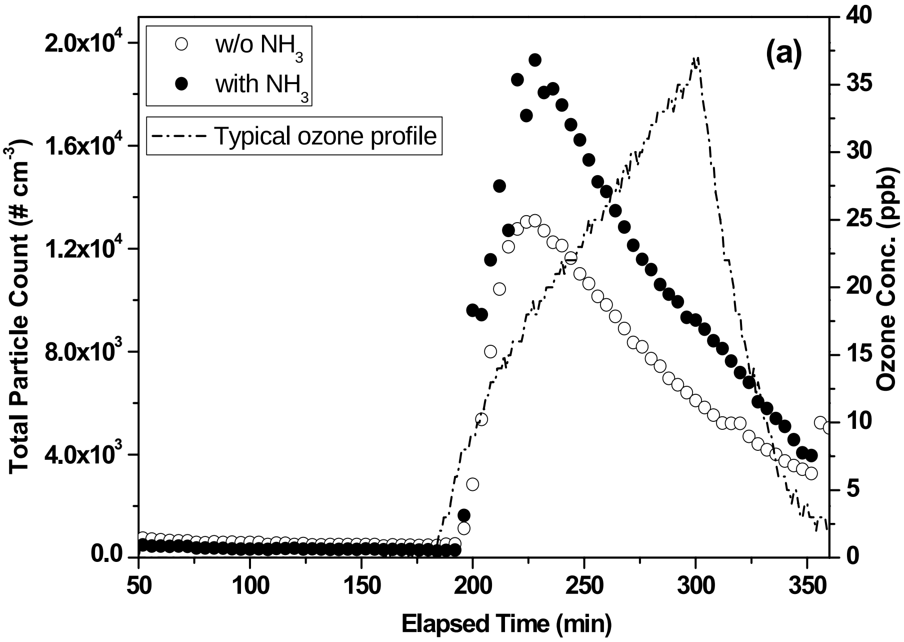


Figure 7- 1. Temporal evolutions of particle size distributions with a diameter of 6-225 nm measured with the SMPS equipment (a) without NH_3 presence and (b) with NH_3 presence in the initial chamber atmosphere.


(a)
○ w/o NH$_3$
● with NH$_3$
Typical ozone profile
Total Particle Count (# cm^{-3})
0.0
4.0x10^3
8.0x10^3
1.2x10^4
1.6x10^4
2.0x10^4
Ozone Conc. (ppb)
0
5
10
15
20
25
30
35
40
50
100
150
200
250
300
350
Elapsed Time (min)

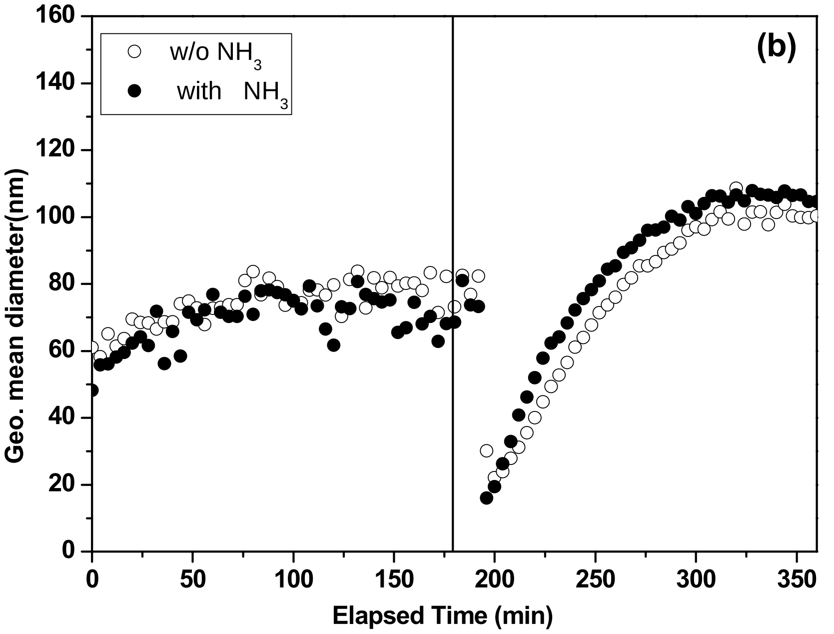
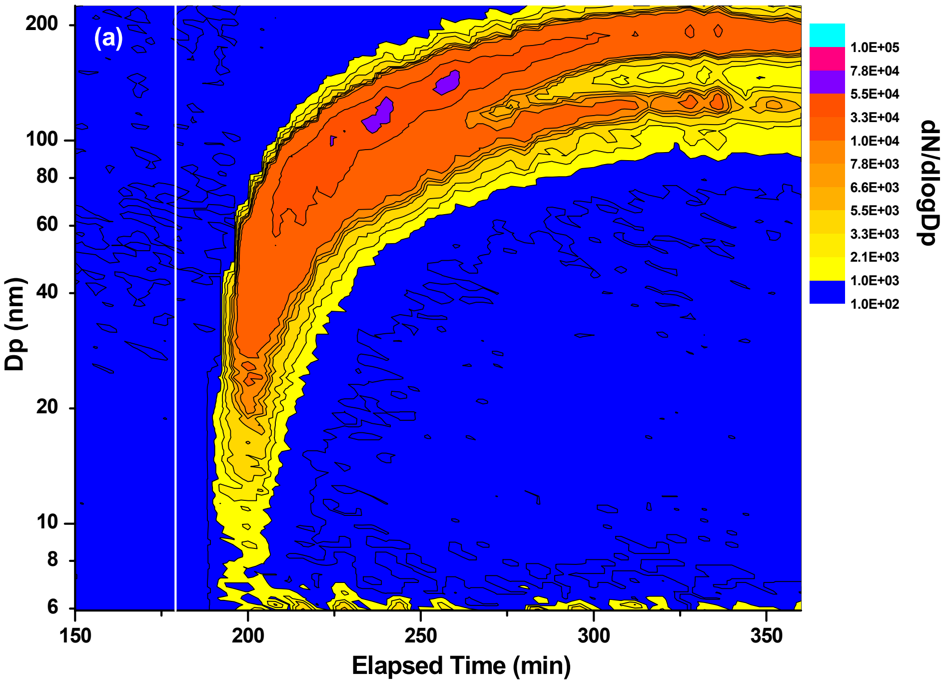
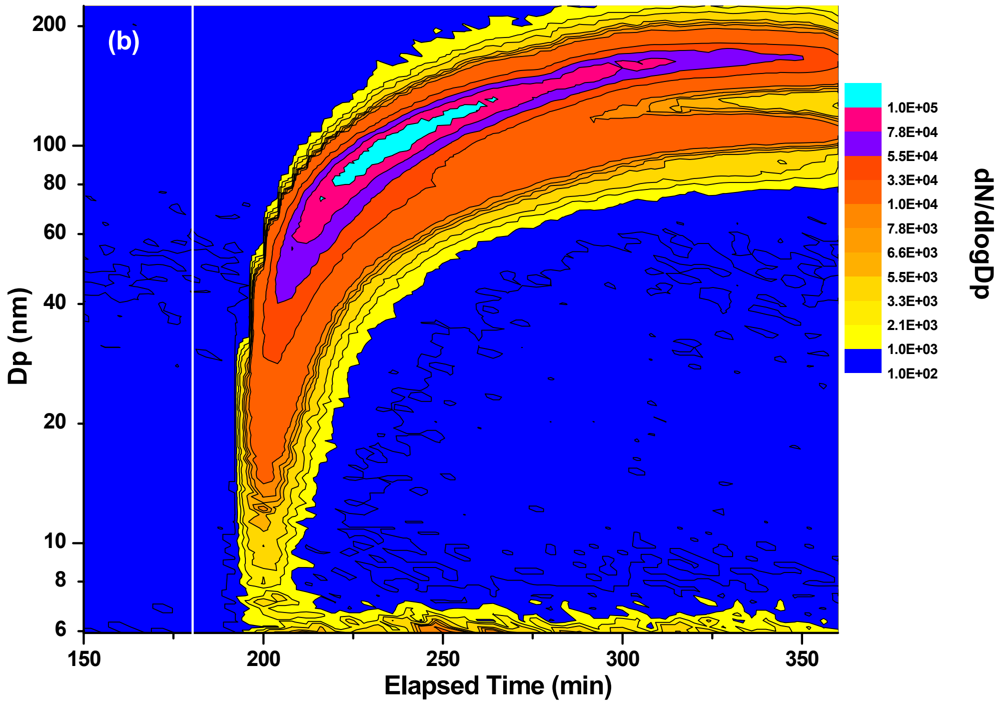
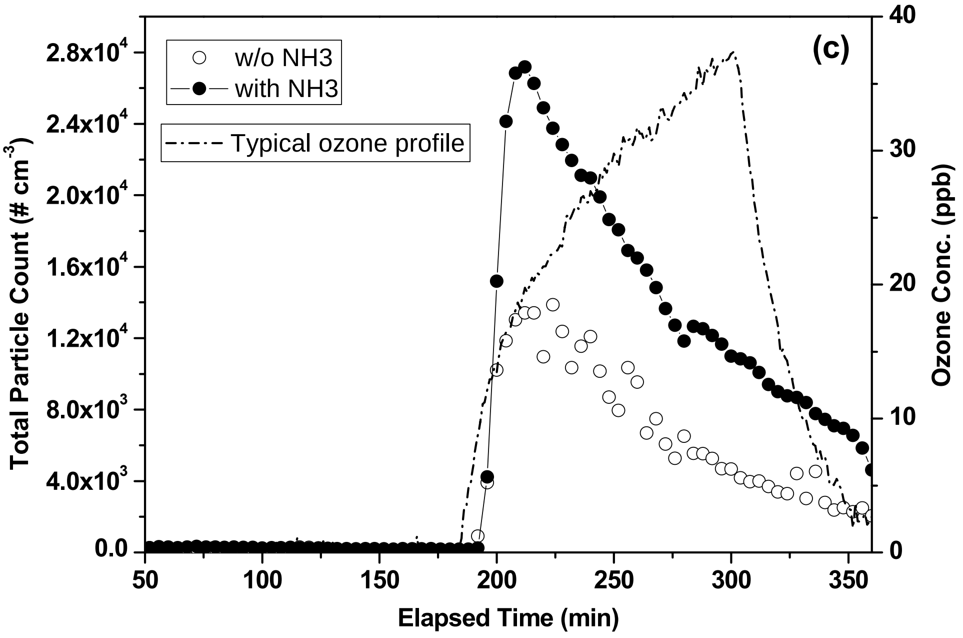

(b)
○ w/o NH$_3$
● with NH$_3$
Geo. mean diameter(nm)
0
20
40
60
80
100
120
140
160
0
50
100
150
200
250
300
350
Elapsed Time (min)

Figure 7- 2. (a) Ozone concentration, total particle number concentration, and (b) geometric mean diameters of SOAs generated from the ozonolysis of BVOCs emitted from floor cleaners without and with NH_3 presence




(b)
Dp (nm)
200
100
80
60
40
20
10
8
6
150
200
250
300
350
Elapsed Time (min)
dN/dlogDp
1.0E+05
7.8E+04
5.5E+04
3.3E+04
1.0E+04
7.8E+03
6.6E+03
5.5E+03
3.3E+03
2.1E+03
1.0E+03
1.0E+02


(c)
w/o NH3
with NH3
Typical ozone profile
Total Particle Count (# cm^{-3})
2.8x10^4
2.4x10^4
2.0x10^4
1.6x10^4
1.2x10^4
8.0x10^3
4.0x10^3
0.0
Ozone Conc. (ppb)
40
30
20
10
0
50
100
150
200
250
300
350
Elapsed Time (min)

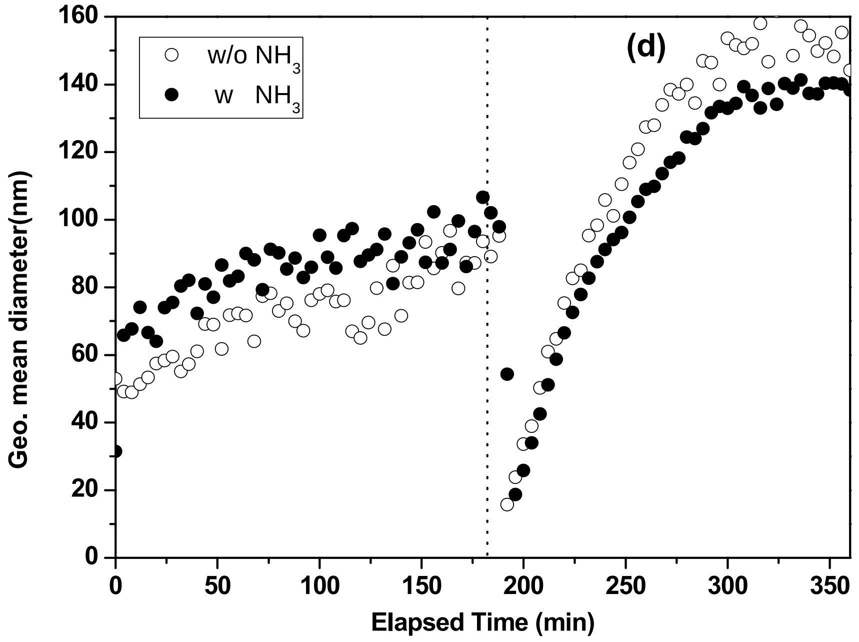
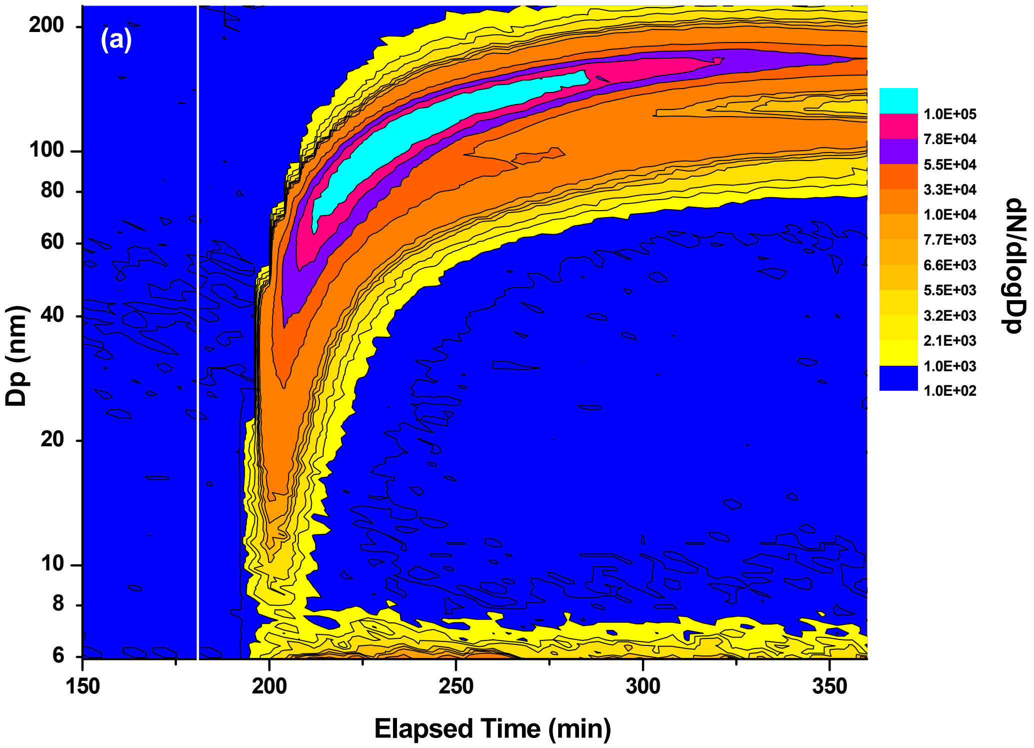
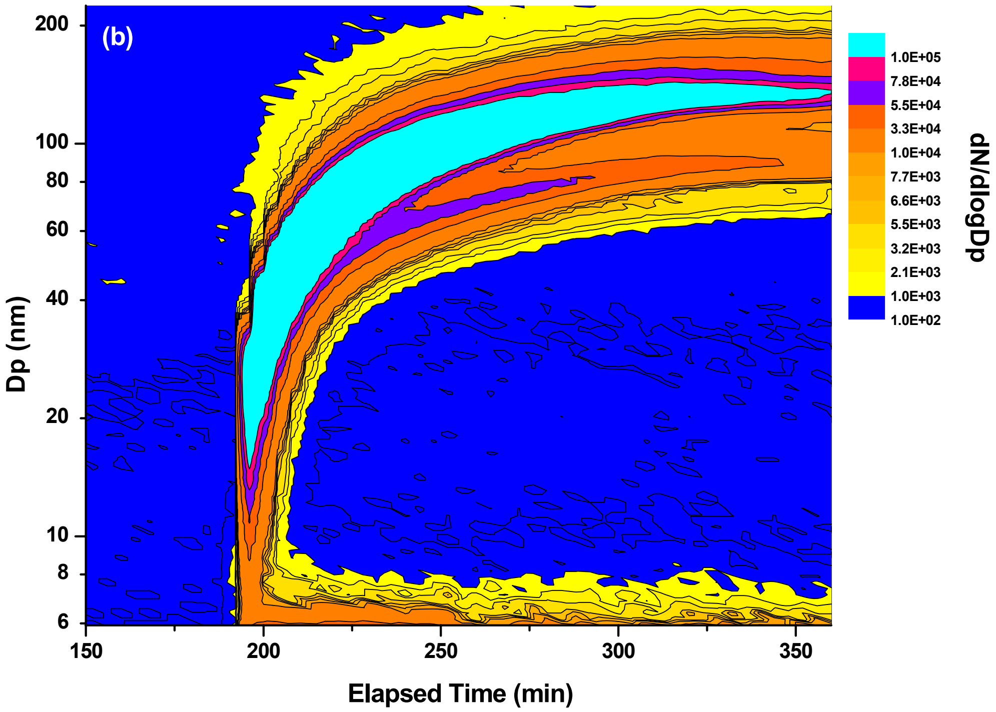
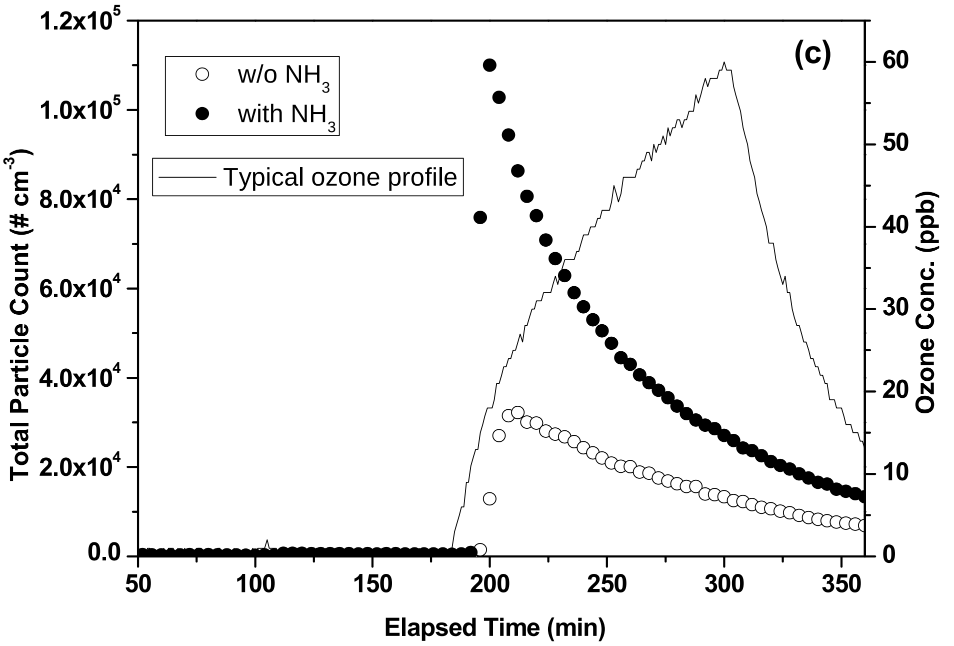


Figure 7- 3. Effect of NH_3 on particle size distributions ((a) and (b)), (c) total particle number concentration and (d) geometric mean diameters of SOAs from the ozonolysis of BVOCs emitted from kitchen cleaners (KC)


(a)
Dp (nm)
200
100
80
60
40
20
10
8
6
150
200
250
300
350
Elapsed Time (min)
1.0E+05
7.8E+04
5.5E+04
3.3E+04
1.0E+04
7.7E+03
6.6E+03
5.5E+03
3.2E+03
2.1E+03
1.0E+03
1.0E+02
dN/dlogDp


(b)
Dp (nm)
200
100
80
60
40
20
10
8
6
150
200
250
300
350
Elapsed Time (min)
1.0E+05
7.8E+04
5.5E+04
3.3E+04
1.0E+04
7.7E+03
6.6E+03
5.5E+03
3.2E+03
2.1E+03
1.0E+03
1.0E+02
dN/dlogDp


(c)
○ w/o NH_3
● with NH_3
Typical ozone profile
Total Particle Count (# cm^{-3})
$1.2x10^5$
$1.0x10^5$
$8.0x10^4$
$6.0x10^4$
$4.0x10^4$
$2.0x10^4$
0.0
Ozone Conc. (ppb)
60
50
40
30
20
10
0
50
100
150
200
250
300
350
Elapsed Time (min)

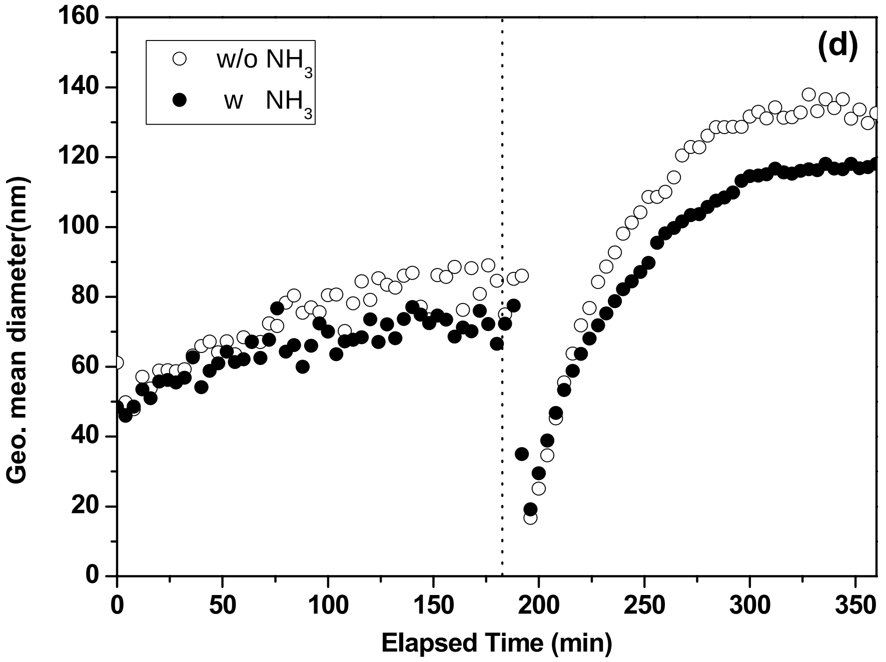
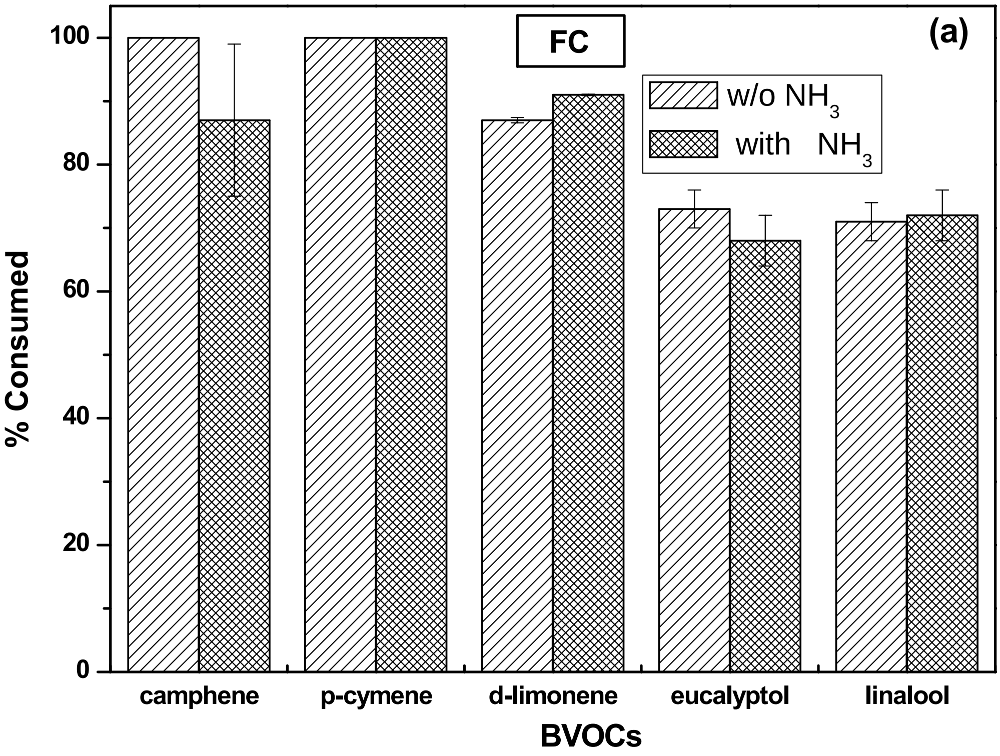
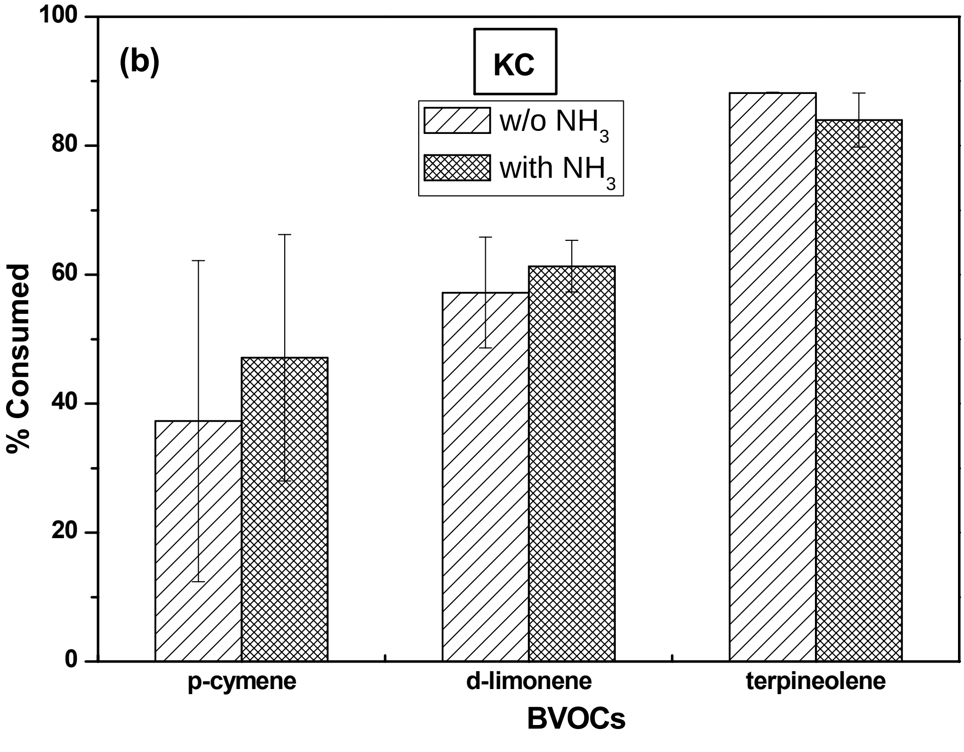

(d)
○ w/o NH_3
● w NH_3
Geo. mean diameter(nm)
160
140
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
Elapsed Time (min)

Figure 7- 4. Effect of NH_3 on particle size distributions ((a) and (b)), (c) total particle number concentration and (d) geometric mean diameters of SOAs from the ozonolysis of BVOCs emitted from dishwashing detergents (DD)


FC
(a)
w/o NH3
with NH3
% Consumed
0
20
40
60
80
100
camphene
p-cymene
d-limonene
eucalyptol
linalool
BVOCs


(b)
KC
w/o NH3
with NH3
% Consumed
0
20
40
60
80
100
p-cymene
d-limonene
terpineolene
BVOCs

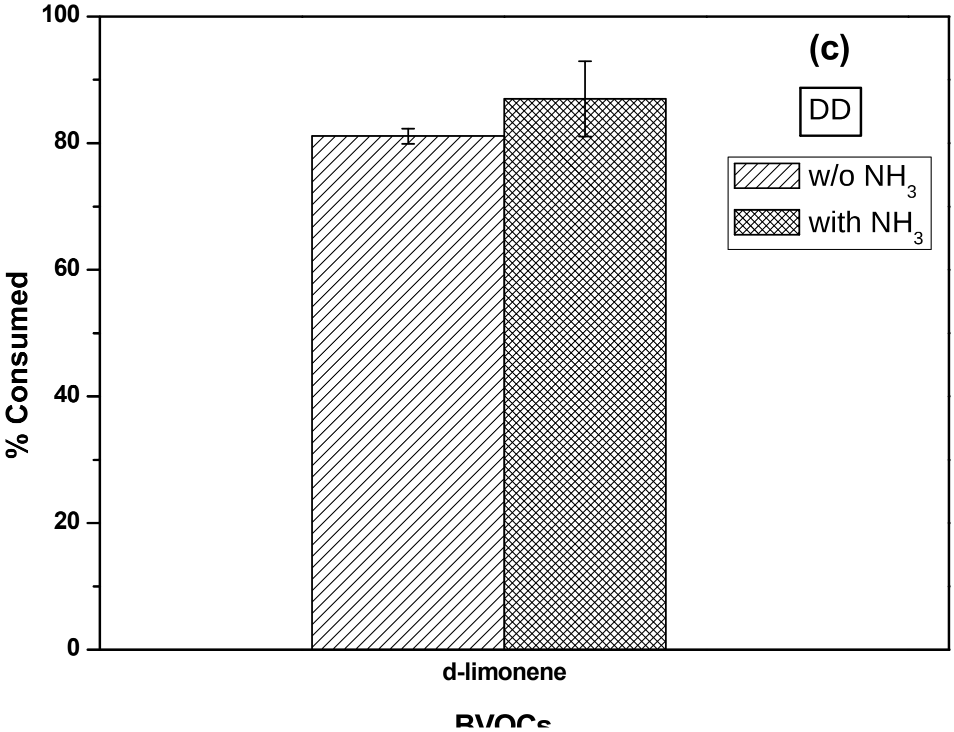
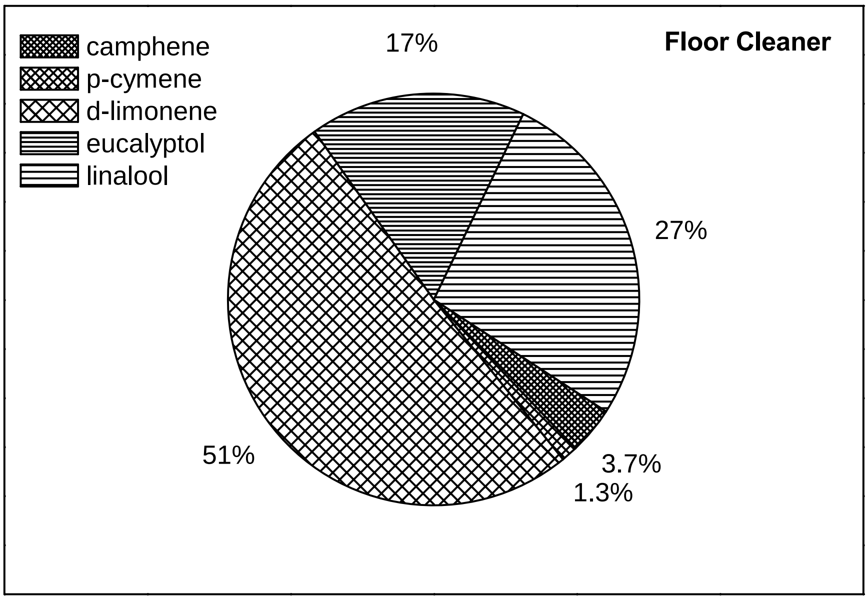


Figure 7- 5. Consumption of BVOCs from floor cleaners (FC), kitchen cleaners (KC) and dishwashing detergents (DD) in the presence and absence of NH_3. Error bars indicated SD (n=3)



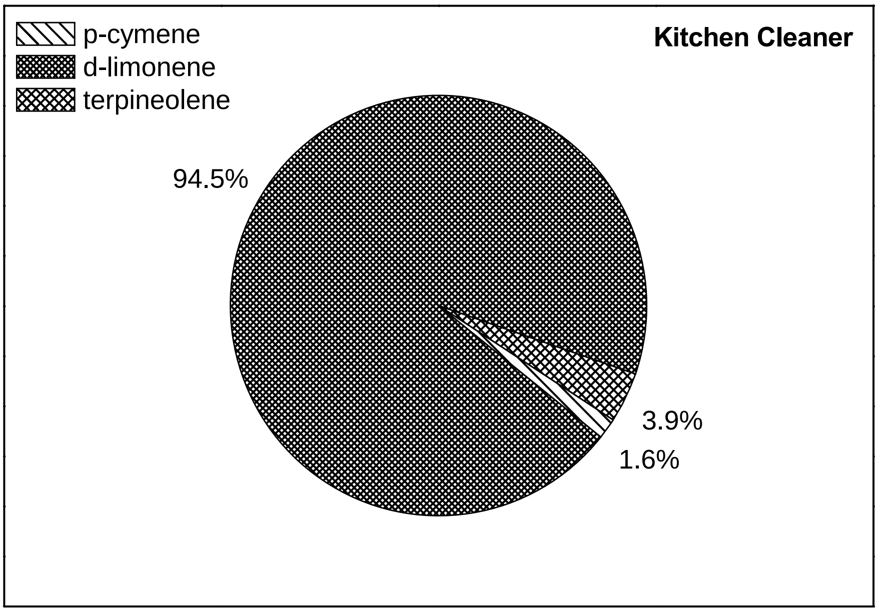
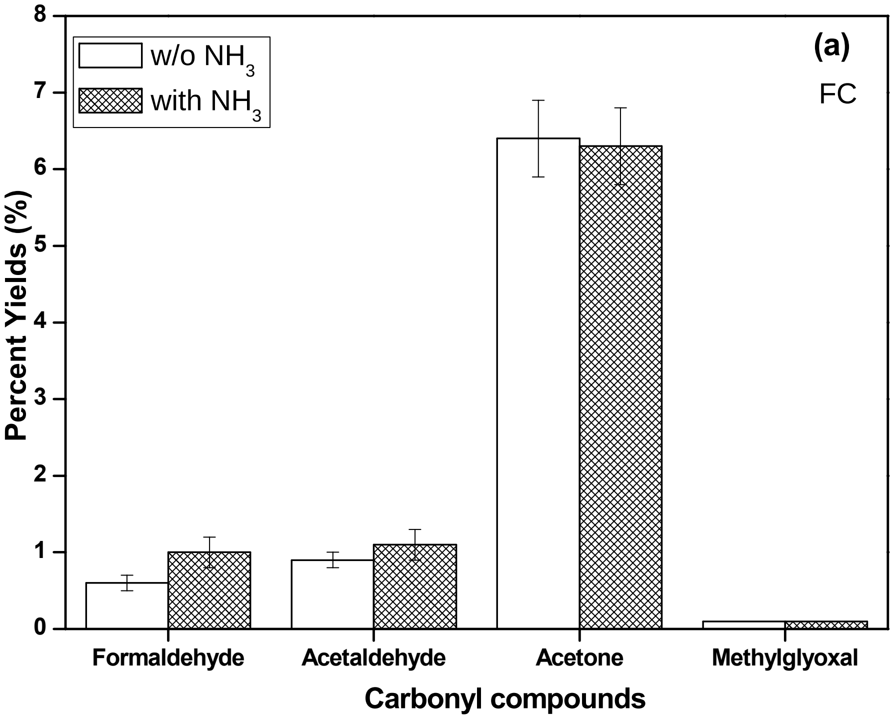
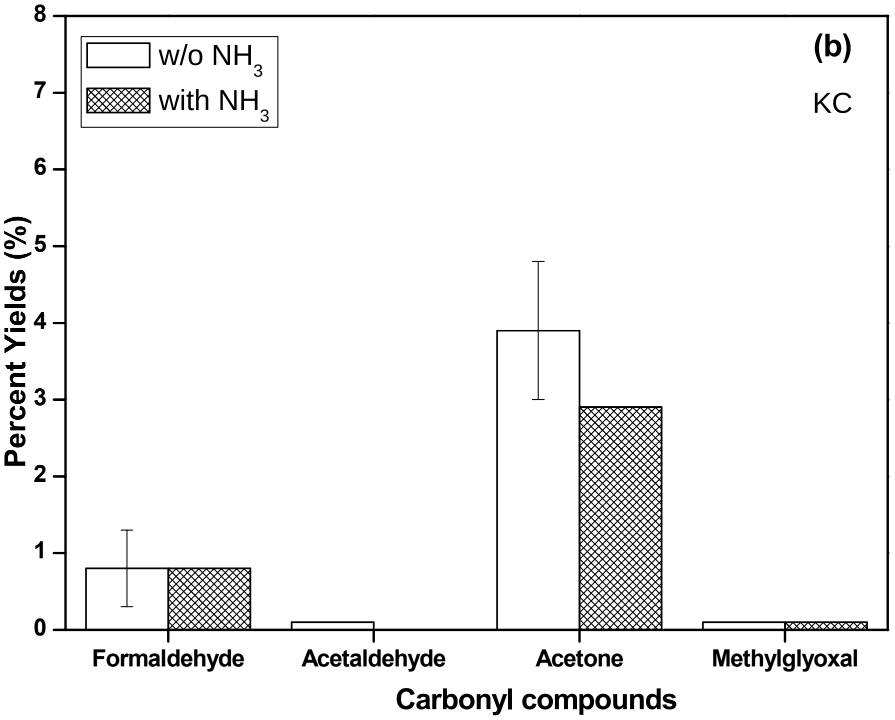


Figure 7- 6. BVOCs fractions in the chamber atmosphere with dosages of floor cleaners and kitchen cleaners before ozone introduction


(a)
FC
w/o NH_3
with NH_3
Percent Yields (%)
0
1
2
3
4
5
6
7
8
Formaldehyde
Acetaldehyde
Acetone
Methylglyoxal
Carbonyl compounds


(b)
KC
w/o NH_3
with NH_3
Percent Yields (%)
0
1
2
3
4
5
6
7
8
Formaldehyde
Acetaldehyde
Acetone
Methylglyoxal
Carbonyl compounds

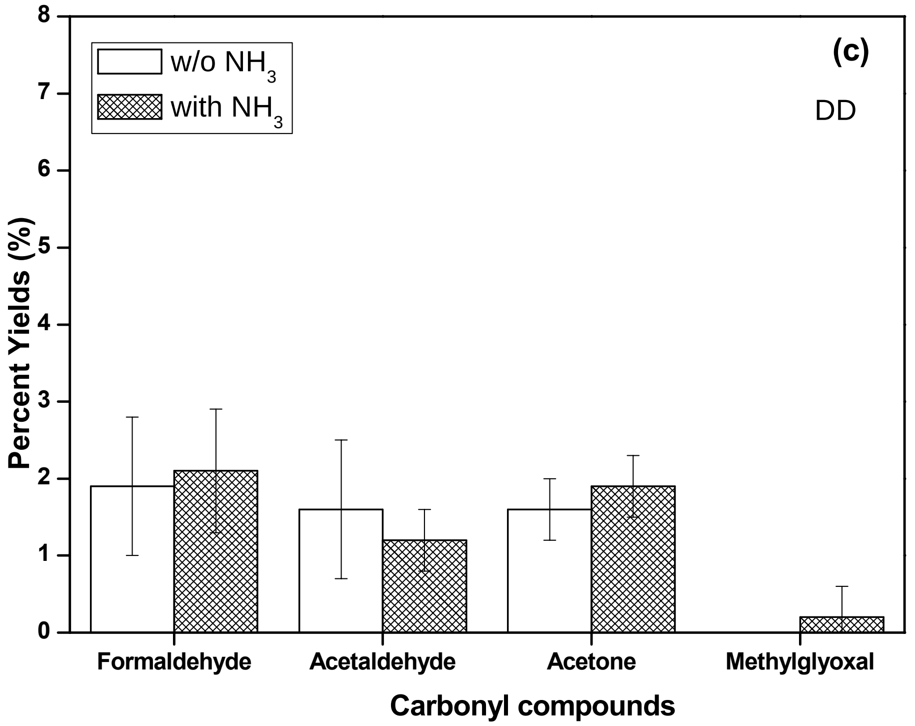


Figure 7- 7. Yields of carbonyl compounds to BVOCs consumption (ppbv/ppbv) in the absence and presence of NH_3

Chapter 8 Conclusions

This research project focuses on ozone-initiated formation of indoor secondary organic aerosols with emissions from cleaning products and air fresheners in a large environmental chamber. The principal objectives are to optimize the solid phase microextraction (SPME) coupled with GC/MS for indoor BVOCs analysis; to determine BVOCs components of cleaning products and air fresheners popularly used in Hong Kong by the optimized SPME-GC/MS method; to evaluate the influences of ACH, T and RH on the secondary pollutants formation from the ozonolysis of BVOCs emitted by household floor cleaner samples; and to investigate the impact of NH_3 on the SOAs formation from the ozonolysis of BVOCs emitted by cleaning products.

SPME-GC/MS method was developed and optimized for the determination of BVOCs. SPME fiber coated with Carboxen-PDMS was adopted to collect 12 BVOCs mixtures under standard conditions with a short exposure time of 5 minutes. Parameters influencing the extraction processes including sampling time, temperature and relative humidity are investigated. All of the target BVOCs were shown to have limit of detections (LODs) in mixing ratios ranged from 0.31 to 0.50 ppbv, which are two magnitudes better than the LODs reported. The method precisions are between 1.1% and 6.7%. Comparison studies were carried out on a set of four floor cleaner extracts using the SPME method and traditional liquid injection method. Good agreement of the target BVOCs by the two methods was demonstrated.

These experimental results indicated that the SPME can serve as a simple and rapid sample collection approach to quantify the BVOCs accurately and precisely in indoor environments.

BVOCs compositions in three categories of cleaning products including FC, KC and DD, and AF were determined by the optimized SPME-GC/MS method. The analysis results demonstrated that chemical composition and concentration of individual BVOC varied broadly with household products in the view of their different functions and scents as indicated on the labels. The concentration of total BVOCs for sample FC1 was the highest up to 4146.0 μg/g, followed by FC2 of 264.6 μg/g, FC4 of 249.3 μg/g and FC3 of 139.2 μg/g. D-limonene was the most abundant detected BVOCs in KC samples with the chemical composition varying from 19.6 ± 1.0 to 1513.0 ± 37.1 μg/g. For dishwashing detergents, only *d*-limonene was detected and quantified. The BVOCs compositions of air freshener samples were much more complicated. It was estimated that the consumption of floor cleaners contributed 51 % of the total BVOCs amount indoors in Hong Kong, followed by air fresheners (42%), kitchen cleaners (5%) and dishwashing detergents (2%).

The effect of physical parameters including ACH, T, and RH on the formation of indoor SOAs through the ozonolysis of BVOCs emitted from floor cleaner was investigated. The total particle count (with D_p of 6-225 nm) was up to 1.2×10^3 # cm^{-3} with ACH of 1.08 h^{-1}, and it became much more significant with ACH of 0.36 h^{-1} (1.1×10^4 # cm^{-3}). This suggests that a higher ventilation rate can effectively dilute indoor BVOCs, resulting in a less ultrafine particle formation. The total particle count increased when the temperature changed from 15 to 23 ^{o}C but decreased when the temperature further increased to 30 °C. It could be explained that high temperature restrained the condensation of formed semi-volatile compounds resulting in low yields of SOAs. When the RH was at 50% and 80%, SOA formation ($1.1 \sim 1.2 \times 10^4$ # cm^{-3}) was more efficient compared with that at RH of 30% (5.9×10^3 # cm^{-3}), suggesting higher RH facilitated the initial nucleation processes. Oxidation generated secondary carbonyl compounds were also quantified. Acetone was the most abundant carbonyl compound. The formation mechanisms of formaldehyde and acetone were also discussed.

We also investigated the effect of NH_3 on secondary pollutants formation from the ozonolysis of BVOCs emitted from cleaning products including FC, KC and DD in a large environmental chamber. Our results demonstrated that the presence of NH_3 can significantly enhance SOAs formation in all the three categories of cleaning products. For example, for the FC sample, the maximum total particle concentration was up to 2.0×10^4 # cm^{-3} in the presence of NH_3, while it was 1.3×10^4 # cm^{-3} without NH_3 , which was 35% lower. However, the extent of NH_3 effect on SOAs formation from the ozonolysis of BVOCs emissions was component-dependent. Additionally, the presence of NH_3 in the reaction systems could increase the consumptions of d-limonene that is the dominant BVOC species as identified in cleaning products. The percent yields (%) of secondary carbonyl compounds generated from ozonolysis of BVOCs emitted from three categories of cleaning products were identified in the presence and absence of NH_3. The formation of condensable salts from reactions between NH_3 and organic acids generated from the ozonolysis of BVOCs attributed to the increase in SOAs particle number concentration.

Chapter 9 Limitations of This Study

The SPME-GC/MS method was developed and optimized to determine BVOCs compositions in clean products and air fresheners used in Hong Kong. BVOCs concentrations in Hong Kong residential homes caused by the consumption of cleaning products and air fresheners were estimated. But there are some limitations in the interpretation of these results because key parameter such as the daily consumption amount was obtained from literature review rather than survey results in Hong Kong. Therefore, one could not generalize the results to present real residential indoor BVOCs concentrations in Hong Kong. It is recommended that local survey results on the consumption amounts of cleaning products and air fresheners in Hong Kong should be obtained and used in future studies.

Although the effect of T, RH and coexistent NH_3 on the formation of indoor secondary products (SOAs and secondary carbonyl compounds) were examined in this study, there are some limitations. Particle number and size distributions were monitored during these experiments, but filter-based samples were not collected due to the low concentrations of SOAs and lack of necessary equipments with high-resolution for further chemical components analysis. For T, RH and coexistent NH_3 effects on the formation of SOAs, it is impossible for us to reveal the reaction mechanisms precisely under different reaction conditions. Therefore, further studies on the analysis of the chemical components of SOAs collected on filters are needed and they are essential to understand the formation pathways of indoor secondary pollutants under different indoor conditions.

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Appendix A: List of Abbreviations

ACH	Air Exchange Rate
AVOCs	Anthropogenic Volatile Organic Compounds
BVOCs	Biogenic Volatile Organic Compounds
CARB	California Air Resources Board
CPC	Condensation Particle Counter
DRI	Desert Research Institute
DNPH	2,4-Dinitrophenylhydrazine
EI	Electron Ionization
ETS	Environmental Tobacco Smoke
GC/MS	Gas Chromatography/Mass Spectrometry
GC/FID	GC with Fame Ionization Detector
HEPA	High-Efficiency Particulate Air
HPLC	High-Pressure Liquid Chromatography
HK EPD	Hong Kong Environmental Protection Department
IAQ	Indoor Air Quality
LOD	Limit of Detection
LOPs	Limonene Oxidation Products
NOELs	No-Observed-Effect-Levels
PM	Particulate Matters
PAQ	Perceived Air Quality
PTR-MS	Proton Transfer Reaction Mass Spectrometry
RH	Relative Humidity
RSD	Relative Standard Deviation
SMPS	Scanning Mobility Particle Sizer
SOA	Secondary Organic Aerosols
SOZ	Secondary Ozonides
SVOCs	Semi-Volatile Organic Compounds
SPME	Solid-phase Microextraction
T	Temperature
TD	Thermal Desorption
THS	Thirdhand Smoke
TSNAs	Tobacco-Specific Nitrosamines
TACs	Toxic Air Contaminants
U.S.EPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds
WHO	World Health Organization