The analysis and monitoring of atmospheric volatile organic compounds via thermal desorption gas chromatography mass spectrometry

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THE ANALYSIS AND MONITORING OF ATMOSPHERIC
VOLATILE ORGANIC COMPOUNDS VIA THERMAL
DESORPTION GAS CHROMATOGRAPHY MASS
SPECTROMETRY**

WONG KEE SHIEN, GWENDELINE

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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fulfillment of the requirement for the degree of
Doctor of Philosophy**

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Summary

An analytical method has been established for the quantitative determination of 48 gaseous volatile organic compounds (VOCs) that were detected in the outdoor environment in Western Singapore by Thermal Desorption Gas Chromatography Mass Spectrometry (TD-GCMS). Tenax/Carbopack X multi-sorbent tubes were evaluated for active sampling performance and the method was validated using VOC standard solutions. The procedure exhibited repeatability with relative standard deviation (%RSD) values $\leq 10\%$, linearity with R^2 values ≥ 0.99 for concentrations from 0.02 to 500 ng, VOC standards breakthrough $\leq 5\%$, tube desorption efficiencies $\sim 100\%$ and the majority of recoveries were between 61% to 120%. 30 mL/min flow rate coupled with sampling volumes of 1 L and 5 L gave the best results for sampling breakthrough and reproducibility during air sampling. Most of the target analytes exhibited acceptable breakthrough $\leq 5\%$, reproducibility $\leq 20\%$ and method detection limits below 0.5 ppbv. The analyte exceptions were pyridine that remained undetected during sampling experiments and dichloromethane that failed the breakthrough requirement.

517 air samples were collected between February 2012 and January 2013 at 30 mL/min for 5 L samples. 60% of the daily trend profiles for hydrocarbons were linked to anthropogenic activities whereas 44% of the carbonyl compounds' intra-day trends were potentially related to biogenic sources. The annual statistical analysis indicated that the VOCs with high maximum concentrations were toluene, 2-methylpentane, hexane, ethyl acetate and styrene. The highest overall maximum concentration is from toluene, at $100 \mu\text{g m}^{-3}$, which is

comparable to Kolkata, India. Monthly box plots revealed that 8 VOCs had their largest monthly averages in September 2012. A major proportion of the target analytes also showed spikes in the monthly means between August 2012 and October 2012, likely attributable to the September 2012 transboundary haze (originating from forest fires in Sumatra, Indonesia). Strong Spearman coefficients of $\rho \geq 0.8$ and $\rho \leq -0.8$ were found between 26 pairs of hydrocarbons and 2 pairs of OVOCs respectively. 3 pairs of hydrocarbons had coefficients of determinations $R^2 \geq 0.8$. Positive matrix factorization (PMF) analysis confirmed 7 source profiles for the modeled hydrocarbons. Health risk evaluation of non-cancer effects was implemented for 16 compounds, while cancer effects were studied for 5 carcinogenic compounds. Benzene had the highest average Hazard Ratio (HR) and Lifetime Cancer Risk (LCR). 44% of benzene HRs were above the potential level of concern. 37% of benzene LCRs were beyond the definite risk of 10^{-4} and the maximum LCR obtained was as high as 6.41×10^{-4} .

Single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes and their carboxylated derivatives (i.e. COOH-SWCNT and COOH-MWCNT) were evaluated for their potential as sorbent materials for trapping and analyzing VOCs using TD-GCMS. The first and subsequent conditioning durations and temperature were optimized for all types of carbon nanotubes (CNT) sorbent tubes to remove organic contaminants prior to usage. The primary artifacts in the CNT blanks were benzene, toluene and hexane. Thermogravimetric analysis (TGA) confirmed that all CNTs were stable when heated at 380°C for several hours during conditioning the different CNTs. Desorption recoveries of 48 VOCs dissolved in methanol and loaded onto the CNTs demonstrated that there were minimal solvent interferences on the adsorption and desorption recoveries of VOCs with different functional

groups. Hydrocarbons and aromatic compounds in MWCNTs had high peak area ratios > 0.7 . 25 to 31 VOCs of varying polarities had peak area ratios > 0.7 when desorbed from SWCNTs, when the solution injection approach was employed for loading. VOCs with electron donor acceptor (EDA) functionalities such as carbonyls, alkenes and alcohols demonstrated poor recoveries on all CNTs, suggesting that they may partake in reactions with residual metal impurities which act as catalysts during high temperature desorption. Inductively coupled plasma-mass spectrometry (ICPMS) experiments led to the detection of high amounts of nickel and molybdenum impurities in all CNTs. The reactions of methanol or formaldehyde with EDA VOCs were deemed to be unlikely due to the absence of an acid medium. Raman spectroscopy offered evidence of defects largely on MWCNTs, indicating that defective sites, together with a large number of methanol molecules could be the reason for high dichloromethane (DCM) breakthrough when using MWCNTs. Both polar molecules (DCM and methanol) can compete for adsorption on defects due to their enhanced affinity for these sites. Exposure to the "normal" analytical laboratory environment revealed that organic contamination of CNT materials likely occurs during transfer of the material in open air and during long-term storage. Desorption profiles from active sampling of atmospheric VOCs showed good agreement with those obtained from the injection of solution standards. SWCNT was established to possess the highest potential as a sorbent material for VOCs analysis using TD-GCMS. The outcomes gave useful insights, expanding the scope of future studies on CNTs.

List of International Refereed Journal Publications

- 1) **G.K.S. Wong**, S.J. Ng, and R.D. Webster, Quantitative analysis of atmospheric volatile organic pollutants by thermal desorption gas chromatography mass spectrometry, *Analytical Methods*, 2013, **5**, 219-230.

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List of Symbols

BP_{Hi}	Air Quality Index Breakpoint $\geq C_p$
BP_{Lo}	Air Quality Index Breakpoint $\leq C_p$
F	Gas Chromatography Column Flow
C_i	Atmospheric VOC Concentration
C_p	Concentration of Pollutant p
D_f	Desorption Flow
DL_j	Detection Limit of j th Species
e_{ij}	Residual Values of the Concentration of the j th Species in the i th Sample
f_{pj}	Mass Fraction Values of j th Species from p th Source
g_{ip}	Mass Contribution (in $\mu\text{g m}^{-3}$) from p th Factor to the i th Sample
HR_i	Hazard Ratio of VOC i
I_D	Intensity of Raman D band
I_G	Intensity of Raman G band
I_{Hi}	Air Quality Index Value corresponding to BP_{Hi}

I_{Lo}	Air Quality Index Value corresponding to BP_{Lo}
I_p	Air Quality Index of Pollutant p
I_{sf}	Inlet Split Flow
LCR_i	Lifetime Cancer Risk of VOC i
m	Number of Samples in the Data Set for PMF modeling
n (Equation 3.1)	Total Number of Samples Collected for Calculation of Sample Mean
n (Equation 3.7)	Number of VOC Species Included in the PMF Model
N_1	Number of VOC Peak Area Ratios in CNT
NO_x	Oxides of Nitrogen
O_{sf}	Outlet Split Flow
p	Number of Factors that Fitted the PMF Model
ρ	Spearman Correlation Coefficients
$PM_{2.5}$	Particulate Matter $<2.5\mu m$
PM_{10}	Particulate Matter $< 10 \mu m$
$Q(E)$	Weighted Sum of Squares in PMF
RfC_i	Reference Concentration of VOC i

R_s	Analytical Resolution
R^2	Coefficients of Determination
s	Standard Deviation of VOC Peak Area Ratios in CNT
t_R	Retention Time
u_{ij}	Uncertainty of the j th Species Concentration (in $\mu\text{g m}^{-3}$) Measured in the i th Sample
UR_i	Inhalation Unit Risk of VOC i
ν	Degree of Freedom
w_h	Peak Width at Half Height
X_i	Concentration Values i of the VOC X
x_{ij}	VOC Concentration (in $\mu\text{g m}^{-3}$) of the j th Species Measured in the i th Sample
$\bar{X}$	Sample Mean of VOC X
$\bar{x}_1$	Mean VOC Peak Area Ratios of CNT 1
$\bar{x}_j$	Geometric Mean of the Samples Greater than Method Detection Limit of the j th Species
Y_i	Concentration Values i of the VOC Y
$\bar{Y}$	Sample Mean of VOC Y

(Peak area ratio)_{VOC}

Normalized Peak Area Ratio of the VOC

(VOC peak area)_{CNT}

VOC Peak Area from the CNT Sorbent

(VOC peak area)_{Tenax/carbopack X}

VOC Peak Area from the Tenax/Carbopack X Tube

List of Abbreviation

AQI	Air Quality Index
ATDSR	Agency for Toxic Substances and Disease Registry
BFB	Bromofluorobenzene
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
CFCs	Chlorofluorocarbons
CNT	Carbon Nanotubes
COOH-MWCNT	Carboxylated Multi-Walled Carbon Nanotubes
COOH-SWCNT	Carboxylated Single-Walled Carbon Nanotubes
CVD	Catalytic Chemical Vapor Deposition
DCM	Dichloromethane
ECTD	Extended Cold Trap Dehydration
EDA	Electron Donor Acceptor
EEA	European Environment Agency
EPA	United States Environment Protection Agency
GC	Gas Chromatography

GCFID	Gas Chromatography Flame Ionization Detector
GCMS	Gas Chromatography Mass Spectrometry
GCPID	Gas Chromatography Photo Ionization Detector
HPLC	High Performance Liquid Chromatography
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IARC	International Agency for Research on Cancer
IRIS	EPA Integrated Risk Information System
LE	Liquid Extraction
LE-GCMS	Liquid Extraction Gas Chromatography Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
MDL	Method Detection Limits
MQL	Method Quantification Limits
MRLs	Minimum Risk Levels
MS	Mass Spectrometer
MWCNT	Multi-Walled Carbon Nanotubes
NEA	National Environment Agency

NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NMHCs	Non-Methane Hydrocarbons
NMVOCs	Non-Methane Volatile Organic Compounds
OEHHA	California Office of Environmental Health Hazard Assessment
OVOCs	Oxygenated Volatile Organic Compounds
PAHs	Polycyclic Aromatic Hydrocarbons
PBM	Probability-Based Matching
PCBs	Polychlorinated Biphenyls
PEA	Polyester Aluminum
PFTBA	Perfluorotributylamine
PIE	Pan-Island Expressway
PM	Particulate Matter
PMF	Positive Matrix Factorization
PSI	Pollutants Standard Index
RELs	Reference Exposure Levels
SPMS	School of Physical and Mathematical Sciences building

SWCNT	Single-Walled Carbon Nanotubes
sSWCNT	Short-length Single-Walled Carbon Nanotubes
TD	Thermal Desorption
TD-GCMS	Thermal Desorption Gas Chromatography Mass Spectrometry
TGA	Thermogravimetric Analysis
THPDS	Tsinghua Passive Diffusive Sampler
TIC	Total Ion Current
VOCs	Volatile Organic Compounds
VMS	Volatile Methylsiloxanes
WHO	World Health Organization
%RSD	Percentage Relative Standard Deviation

Introduction

1.1 Introduction

Air pollution is a major problem that partly exists due to continual urban and industrial development. The consequence of releasing hazardous contaminants into the atmosphere can have far-reaching effects as these unconfined substances can be transported extensively to other places by the dynamic movement of air. The result of chronic inhalation of toxic pollutants has severe health implications and may result in premature mortality. According to a recent international study, more than 2.1 million deaths worldwide were attributed to outdoor air pollution annually [1]. The figure is almost twice the previously reported 1.3 million by the World Health Organization (WHO) [2]. Exposure to atmospheric pollution is inevitable and not within the control of most individuals. Hence, legislative measures have to be implemented by government agencies at both the national and international levels. This includes evaluating the concentration of chemicals, particulates and biological materials.

Six criteria pollutants namely: Particulate matter (PM), oxides of nitrogen (NO_x), carbon monoxide (CO), sulfur dioxide (SO₂), lead and tropospheric ozone (O₃), are usually employed as indicators for monitoring air pollution by various environmental authorities and regulatory boards globally [3-7]. Various types of air quality indices are calculated based on

the concentration of criteria pollutants and used for interpreting the toxicity of the ambient conditions. In North America, the United States Environmental Protection Agency (EPA) calculates the Air Quality Index (AQI) based on all mentioned pollutants, using a linear interpolation equation (equation 1.1):

$$I_p = \frac{I_{Hi} - I_{Lo}}{BP_{Hi} - BP_{Lo}} (C_p - BP_{Lo}) + I_{Lo} \quad \text{-----} \quad (1.1)$$

Where I_p is the index of pollutant p , C_p is the concentration of pollutant p , BP_{Hi} is the breakpoint that is greater than or equal to C_p , BP_{Lo} is the breakpoint that is lower than or equal to C_p , I_{Hi} is the AQI value corresponding to BP_{Hi} and I_{Lo} is the AQI value corresponding to BP_{Lo} [8]. The AQI is a numerical value used by the EPA to communicate to the public the severity of the air pollution. In Singapore, the National Environment Agency (NEA) computes the Pollutants Standard Index (PSI) using the same equation except that it is based on five pollutants [9]. Particulate matter $<2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) and lead are excluded from the calculations.

Primary emphasis on these air contaminants is becoming inadequate to safeguard public health and to protect the natural environment. Atmospheric Volatile Organic Compounds (VOCs) is a class of pollutants that is becoming increasingly important due to the scale of globalization and industrialization over the last few decades. VOCs are defined as a wide class of organic compounds containing up to 15 carbon atoms that have vapor pressures greater than 10 Pa at 25 °C and boiling points up to 260 °C [10]. These compounds are found to be precursors for the production of tropospheric O_3 , which is one of the main contributors to photochemical smog [11-13]. In addition to their roles in photochemical oxidations, they are also involved in stratospheric O_3 depletion and greenhouse effects [14-16]. VOCs are also

detrimental to human health. Acute exposures to VOCs could stimulate dyspnea, aemesis, epistaxis and nausea [17]. Long-term exposures include renal failure, cirrhosis, disorders to the central nervous system, respiratory diseases and various types of cancers [18, 19].

Some countries have incorporated Non-Methane Volatile Organic Compounds (NMVOCs) as criteria ambient contaminants for routine screening [20, 21]. In the European Union, regulations were imposed to limit the average benzene concentration in air to $5 \mu\text{g m}^{-3}$ [22]. However, unlike the six common pollutants, the acceptable concentration levels for different types of VOCs in the natural environment are still unknown. There is a lack of established data to determine the permissible levels of VOCs that are not harmful to the environment and human health in order to develop legislations and protocols to control their emissions.

Gas Chromatography Mass Spectrometry (GCMS) is by far the best and the most common analytical technique for determining the amounts of VOCs present in the air [23]. Liquid extraction (LE) is the conventional preparation step, coupled with GCMS [24]. Activated charcoal is utilized for sampling VOC molecules, whereas carbon disulfide, is used as the extracting solvent for desorbing these VOCs retained on the charcoal [25-27]. There are several limitations in using LE-GCMS. The method is known to have lower sensitivity (i.e. higher limits of detection) compared to other VOC analytical methods because a solvent is required which will inevitably dilute the sample [24-27]. Carbon disulfide is extremely hazardous if not used correctly because it attacks the central nervous system [28, 29]. In addition, polar and reactive species from the charcoal cannot desorb efficiently in polar and aqueous environments because of numerous strong binding interactions, resulting in permanent adsorptions and catalytic reactions of target compounds into different products [24, 30, 31].

Thermal Desorption (TD) is a solvent-free alternative to liquid extraction. VOCs can be collected using various types of sampling vessels such as sorbents, canisters or polymer bags. These sampling vessels would be connected to the GCMS via a TD system which has a focusing mechanism to concentrate the VOCs before transferring them into the GCMS for analysis. The TD process employs high purity inert gas, usually helium, for high temperature extraction. There are two stages in TD for sorbent-based sampling techniques. The first stage involves transferring the VOCs from the air sample to the preconcentrator. The preconcentrator is either an electrically-cooled Peltier trap or a cryogenic trap. High temperature and a stream of helium are applied to the tube to desorb VOCs and transfer them into the trap for preconcentration. The final stage would involve the inversion of helium flow through the trap and the heating of the cold trap rapidly to a high temperature at the maximum rate to transport the VOCs into the GCMS. Figure 1.1 shows the TD mechanism for sorbent-based sampling.

Figure 1.1: Two stages of thermal desorption processes for sorbent tube sampling.

Figure 1.2: Summary flowchart of the advantages and limitations of several sampling methods [33, 34].

As for canister and polymer bag sampling, a multiple cryofocusing or cold trap system is needed to remove water and carbon dioxide before GCMS analysis. TD is required to transport analytes from one preconcentrator to another, while removing moisture and permanent gases during each step. An aliquot of air from the sampling container is injected into the first preconcentrator directly [32]. The final TD step is the same as mentioned for sorbent-based sampling. In this chapter, various solvent-free sampling methods that can be used in conjunction with Thermal Desorption Gas Chromatography Mass Spectrometry (TD-GCMS) will be reviewed from the literature for the last six years, as well as the different types of sorbent materials that are commercially available for sorbent-based sampling procedures (i.e. active and passive sampling). Figure 1.2 is a flowchart summarizing the advantages and disadvantages of the various sampling techniques that will be covered in

various sections. There will also be sections to compare atmospheric VOC profiles from around the world and discuss on the latest developments of new analytical methods for screening atmospheric VOCs.

1.2 Whole Sampling Methods

Whole air sampling is the collection of air by using tightly-sealed containers such as bags made of highly durable polymers or stainless steel canisters. Air enters the vessel by free or applied movement (i.e. vacuum) [33]. Prior to analysis, enrichment of VOCs is carried out using a cold trap to enhance the sensitivity of the method. It is the easiest sampling method and has several advantages to other sampling procedures. Unlike sorbent-based sampling, multiple analyses can be performed on one sample by injecting aliquots of air from the sampling device into the TD-GCMS [34]. There are no breakthrough problems when sampling with containers. Thus, these procedures can be used to accurately determine the quantities of extremely volatile organic compounds such as acetylene, the lightest perfluorinated compounds and a few permanent gases (N_2O , H_2S and SF_6) that are compatible to TD-GCMS analysis [35]. However, thorough cleaning of containers is essential to minimize contamination and losses. One major limitation of whole sampling is the high cost required for transporting the heavy containers as well as the equipment for cleaning the vessels. In this section, sampling with polymer bags and canisters will be discussed and recent publications will be reviewed.

1.2.1 Polymer Bags

Polymer bags are less costly compared to stainless steel canisters and are offered in a wide range of volumes. Different types of polymer bags are also commercially available such as

Tedlar, Teflon and Nalophan. The most commonly used polymer bag for sampling is Tedlar bags [36]. Tedlar bags are polyvinyl fluoride bags manufactured and marketed by DuPont [37]. They are in compliance to the EN 13725 of the European Committee for Standardization and are approved by the EPA in several of its compendium methods such as TO-3, TO-12, TO-14A, TO-15 [38, 39]. These bags are reusable but have to be cleaned rigorously using ultrapure inert gases or air. However, repeated bag usage is not highly recommended for a prolonged period of time, as micro-damages and scratches from mechanical stress to the polymer material during the handling of samples can alter the polymer film structure and the inertness of the material [40].

Some common problems associated with Tedlar bag sampling were highlighted in recent publications. Mochalski and coworkers evaluated the stability of 41 compounds found in human breath and determined that contaminants such as phenol and N,N-dimethylacetamide were emitted by the bag and detected during background tests [41]. In addition, long storage of air sampled in Tedlar bags is usually not possible. The maximum storage stability is reduced due to losses or contamination by diffusion through the walls of the polymer structure. Alonso et al. reported a 5% loss of 2,5-dimethylfuran in Tedlar bag samples after 3 hours of storage [42]. Beauchamp and colleagues employed on-line proton-transfer-reaction mass spectrometry to study the storage capabilities of Tedlar bags for alcohol, nitrile, carbonyl, terpene and aromatic compounds over a 70 hour storage period [36]. The results indicate that sufficient sample authenticity replication is achieved when samples were analyzed within 10 hours of sampling [36].

The target analytes are also a factor in the selection of polymer bags since diffusion can occur for certain types of compounds due to the permeability of the material. Kim and

coworkers [43] compared the stability of polyester aluminum (PEA) and Tedlar for eight VOCs by varying the storage times, analyzing them at three time intervals and calculating the relative recoveries after each time period. PEA demonstrates higher relative recoveries and thus greater stabilities compared to Tedlar for a long storage period of 72 hours. Methyl isobutyl ketone is the only compound that exhibits excellent relative recoveries in both PEA and Tedlar, while isobutyl alcohol had the most significant difference in recovery values between both bags with 94% and 31% respectively.

As mentioned in the previous paragraph that some molecules can permeate through the polymer material, water is one such compound that has the ability to do so. To minimize the influence of the external humidity on the levels of moisture present in the collected sample, Cariou and Guillot [44] developed a double-layered Tedlar bag with a stainless steel valve. Drying agents were added in between the two films to absorb water and retain the dryness of the air sample for an extended period of time.

Another alternative to a double-film polymer bags with desiccants is a sample moisture removal procedure using the principles of humidity diffusion established by Beghi and Guillot [45]. Tedlar, Teflon and Flexfoil sampling bags containing a mixture of 10 VOCs at 500 ppb in a 70% relative humidity atmosphere were placed in a chamber and subjected to flushing with a stream of dry air at less than 5% relative humidity. Tedlar has the highest rate of water diffusion and thus the samples in the Tedlar bags were dry (relative humidity < 5%) after a few hours and did not show significant VOC loss. The same pretreatment was tested again using Nalophan and compared to Tedlar, at a low concentration of $10 \mu\text{g m}^{-3}$ for 11 VOCs. As the humidity diffusion rate is higher for Nalophan compared to Tedlar, the relative

humidity in a 10 L air sample decreases from 80% to 20% in 2 hours at 20 °C and no significant losses were observed for all studied VOCs [46].

The preconcentration process for Tedlar bags is identical to the one used for canisters. It has a far more complicated mechanism compared to the trap method used in sorbent-based sampling because the removal of water vapor and carbon dioxide are essential before analysis of the air matrix can take place. More details about moisture elimination will be discussed under the canisters section.

1.2.2 Canisters

There are two types of canister sampling methods. Grab canister sampling is performed by filling the canisters immediately with whole air. Time-integrated canister sampling is carried out by collecting air with a flow controller or a critical orifice assembly [39]. Although the costs of canisters are much higher than polymer bags, air samples stored in canisters are stable for a longer period of time compared to bags [47]. The stability of VOCs in canisters is due to the electropolishing procedures or inert coating methods that are employed for deactivating active sites on the inner walls of the canisters.

To prevent reactions within the canisters' interior, the internal surfaces are usually covered with a chromium-nickel oxide layer via Summa Passivation or chemically coated with fused-silica [34]. Fused silica canisters are believed to be more inert than the conventional Summa passivated cannisters based on the results of a study that explored the stability of 58 VOCs in both types of canisters [48]. Recent publications on samplings with fused silica canisters include the validation of the vacuum canister method for determining; (i) ppb levels of 7 VOCs that are stimulants in war agents based on the National Institute for Occupational

Safety and Health (NIOSH) guidelines reported by Coffey and coworkers [49] and, (ii) the quantitative analysis of VOC species in Kaohsiung City in Taiwan to describe their vertical and diurnal variations at different levels from the ground reported by Lin et al. [50]. Passivated canisters coupled with Gas Chromatography Flame Ionization Detector (GCFID) were used for quantifying 22 VOCs in 48 air samples in a recent report by Lai and coworkers [51] to apportion their source profiles and contributions at the Taipei International Airport.

Vacuum glass canisters are recently developed air containers that are economically comparable to polymer bags and simultaneously retain the inert capabilities of stainless steel canisters. These sampling devices were validated for sampling 14 VOCs in indoor environments at ppb levels by LeBouf et al. [52]. All analytes remained stable over a period of a month at ppb levels, with 13 of the 14 VOCs meeting all validation requirements, demonstrating their suitability as sampling vessels for storage and analysis.

Similar to polymer bags, preconcentration using canisters take place before introduction into the GCMS. The preconcentration mechanism involves trapping target VOCs, water management and on-column focusing. There are three main types of water management methods that are employed in preconcentration systems: permeation drying, extended cold trap dehydration (ECTD) and microscale purge and trap. Older water management techniques such as permeation drying are rarely in use nowadays due to the advancements of improved water management techniques that offer better recoveries for a wider range of compounds. Permeation drying is carried out by using a Nafion membrane to absorb moisture. Sulfonic groups on the Nafion are swiftly hydrated and the rates of diffusion of water molecules through the membrane is controlled by the humidity on either sides of the membrane [53]. The method is suitable for non-polar analytes but not for species with polar

Figure 1.3: Three-trap preconcentration system based on extended cold trap dehydration for analysis of canister samples.

groups and reactive functionalities [54]. ECTD offers higher recoveries than Nafion drying for a wider variety of VOCs with different polarities.

It occurs with the removal of moisture by introducing the sample into the first trap at -40 °C to -50 °C to freeze all water vapor present in the sample, but allowing VOCs to bypass the first trap and enter the second trap containing a weak sorbent material [55]. The step is repeated at other temperatures for the removal of permanent gases and carbon dioxide (CO₂). This moisture and CO₂ removal is based on the principles of the vastly different saturation points of water, carbon dioxide, permanent gases and VOCs in air. Some of the heavier VOCs that condense in the first cold trap are transferred to the second cold trap by warming the first trap to slightly above the melting point of water, followed by purging with a small amount of inert gas. Figure 1.3 shows water and permanent gas removal by ECTD

Figure 1.4: Three-trap preconcentration system based on microscale purge and trap for analysis of canister samples.

using a typical three-trap system. Rice et al. [56] reported an analytical method for determining the isotopic composition of formaldehyde using stainless steel canisters for grab sampling. A customized four-trap preconcentration system based on the principles of cold trap dehydration was used for removing humidity and other permanent gases. Gas chromatography isotopic mass spectrometry was employed for analysis.

Microscale purge and trap is very similar to ECTD. Figure 1.4 depicts the process in a three-trap system. The main difference is that it involves an initial collection of water, carbon dioxide and VOCs together into a cryogenic trap kept at extremely low temperature around -150°C to remove other permanent gases, followed by low helium purge and slow heating to between 10°C to 20°C for two purposes; (i) to desorb and transport VOCs and carbon

dioxide into a secondary focusing mechanism for further preconcentration and removal of CO₂, and (ii) to retain frozen water vapor in the cryogenic trap [55, 57].

Hoshi et al. reported the sampling of 54 hydrocarbons in the Tokyo metropolitan area using microscale purge and trap for water removal. Air samples were preconcentrated three times; firstly into a glass bead cryogenic trap at -155 °C, heated to 20 °C and transported into a secondary Tenax trap at -15 °C and lastly, a back-flush at 180 °C for further focusing on the capillary trap before injection into the GC column [58]. Microscale purge and trap is more expensive than ECTD due to the higher consumption of liquid cryogen for the traps.

1.3 Sorbent-based Sampling Methods

Sorbent-based samplings are conducted by retaining VOCs that are present in the air onto sorbents packed in a stainless-steel or glass tube. Figure 1.5 illustrates the insides and the packing of a multi-sorbent tube. The adsorption mechanisms of VOCs onto sorbent surfaces are based on chemical reactions and physical adsorption. Sorbents with large surface areas have pores with molecular-scale sizes, capable of mechanically trapping or chemically interacting with VOC analytes [59]. Porosity dimensions are categorized according to macropores (> 50 nm wide), mesopores (> 2 nm but < 50 nm in diameter) and micropores

Figure 1.5: Illustration of the insides of a multi-sorbent tube.

(<2 nm in width) by the IUPAC [60-62]. Sorbents such as Chromosorb contain sufficiently large pores for chemical reactions to take place. Chemical adsorption involves sorbents acting as supports for chemical molecules to react with one another to form a more stable product. Activation energies of these reactions could be possibly reduced during chemisorption, resulting in the occurrence of chemical reactions [59].

Physical adsorption processes vary according to the porosity dimensions. Adsorption taking place on microporous structures result in the adsorbates being retained by much stronger forces as they are in proximity to several sides of the pore interior. The mechanism can be expressed using the Langmuir or Dubinin–Radushkevich equation [59, 63]. As for other types of pores, the adsorption behavior is accounted for using the Freundlich or Langmuir isotherm. Macropore adsorption behavior are attributed to molecular coverage (monolayer) followed by the accumulation of further layers (multilayer) [64]. At extremely low atmospheric concentrations of contaminants, the process is explained by the linear region of the Freundlich isotherm and retention volumes can be employed to estimate safe sampling volumes [65-67] . High ambient VOC concentrations however, correspond to the curved section of the Freundlich isotherm where breakthrough becomes a variable dependent on concentration [68-74].

Desorption of VOCs is performed by heating the sorbent tube to a high temperature and using a stream of high purity helium to extract and transfer the VOCs into the trap for preconcentration, followed by another desorption by heating the trap to a high temperature together with a backflushed stream of helium to transfer the VOCs into the GCMS. Thus, the sample introduction is named TD due to the usage of heat and inert gas for adsorbate removal from the sorbents in the sample tube and the cold trap. In order to achieve higher peak

resolution and sensitivity enhancement, the cold trap is utilized as an intermediate step for enrichment of VOCs from the sorbent tube [75].

Different types of sorbents have unique physical and chemical characteristics and thus, have different selectivity for various VOC species. Single sorbents are usually insufficient for analyzing a wide range of VOC analytes with varying polarity and volatility [76]. Multi-sorbent tubes and traps are comprised of a few different types of sorbents within the tube that can efficiently adsorb an extensive variety of compounds [77]. Both sorbent tubes and focusing traps are commonly packed with between 1 to 4 types of sorbent materials in order of increasing sorbent strength from the sampling end [78]. The sorbents have to be packed in such an order to prevent permanent irreversible retention or bindings of less volatile analytes onto stronger sorbents[34]. Weaker sorbents can trap these compounds first during sampling and injection of standards without entering the strong sorbents. When selecting sorbent materials in a multi-sorbent tube and trap, the thermal compatibility between sorbent materials matters because the maximum temperature for conditioning the tube has to be based on the sorbent with the lowest maximum temperature without causing decomposition to the material. Various types of commercially available sorbents for air sampling and TD-GCMS analysis are summarized in the following section. In addition, two types of sorbent-based sampling: passive sampling and active sampling will be discussed in detail.

1.3.1 Types of Sorbents for Sampling

There are four main types of sorbent materials. They are graphitized carbon blacks, porous polymers, carbonized molecular sieves and zeolite molecular sieves. Graphitized carbons are generally non-porous and non-specific. As graphitization is utilized to remove selective sites

of adsorption and prevent the generation of hydrogen bonds, small and polar compounds such as water are not strongly retained [34]. Hence, the surfaces of graphitized carbon blacks are very homogeneous and hydrophobic. There are certain exceptional graphitized carbon blacks such as Carbograph 5TD that show microporous behavior and are suitable for sampling very volatile organic molecules such as buta-1,3-diene [79].

Porous polymers are polymeric resins that are formed by suspension polymerization. A mixture of monomers and crosslinking reagents are polymerized in the presence of an inert solvent [80]. There are several different types of commercially available porous polymers used for thermal desorption applications. Chromosorb sorbents are polymers and copolymers derived from divinylbenzene and styrene [81]. Tenax sorbents are types of poly(2,6-diphenyl-*p*-phenylene oxide) based on the oxidation of 2,6-diphenylphenol [59, 82]. Porapak series are polymers and copolymers synthesized from vinylpyrrolidone, vinylpyridine, ethylvinylbenzene, divinylbenzene, ethylene glycol dimethyl adipate and styrene [83].

Carbonaceous molecular sieves are microporous sorbents and are suitable for analyzing very volatile and very low molecular weight organic compounds due to their high surface area. They are prepared by controlled pyrolysis of poly(vinylidene chloride) or sulfonated polymers (Carboxens) [33, 80]. Carbonaceous molecular sieves contain very tiny graphite crystallites crosslinked to yield a disordered cavity aperture structure [80].

Zeolite molecular sieves are artificially created from alkali metal aluminosilicates [80]. Adsorption onto zeolites is dependent on size and the strength of adsorption binding on the interior pore surface and particle surface. Their applications can be very specific. For example, molecular sieve 5 Å is used for monitoring nitrous oxide [79].

1.3.2 Physical and Chemical Properties of Sorbents

Tables 1.1, 1.2 and 1.3 summarize the various commercial sorbents available for thermal desorption applications and their physical and chemical properties: sorbent adsorption strength, hydrophobicity, inertness, thermal stability, friability and artifact formation. Comparisons of the advantages and limitations of sorbent materials are necessary for determining the ideal sorbent materials for an analytical procedure. Sorbent adsorption strength is defined as the ability of the material to retain analytes during sampling and release them upon heating. This is commonly validated by evaluating the amount of VOC that were loss from the sorbent tube (also known as percentage breakthrough), breakthrough volumes or safe sampling volumes.

To determine the VOC mass that is lost from standards injection or sampling, a second sorbent tube is connected in series to the back of the first tube. When VOC standards are injected or when air is sampled into the front tube at a constant gas flow and fixed duration, the amount of VOC that is detected in the back tube should be $\leq 5\%$. Breakthrough volume is determined by connecting the sorbent tube to a mass spectrometer (MS) or FID, based on the VOC retention time, sorbent mass and gas flow through the tube. While breakthrough volumes can be experimentally performed and calculated, validated breakthrough information of some compounds and sorbents are also available from commercial suppliers [79, 84]. Safe sampling volumes can be calculated and has two definitions; either half of the chromatographically evaluated breakthrough volume, or two-thirds the experimentally evaluated breakthrough volume [85]. Another important factor that can affect the analyte retention on the sorbent is relative humidity in the atmosphere. Increased relative humidity can result in higher breakthrough and analyte leakages from the material [24]. It is important

Table 1.1: Physical and chemical characteristics of porous organic polymers [33, 34, 79, 81, 86]. Bp stands for VOC boiling point.

Sorbent	Chemical Composition & friability	Chemical Inertness	Hydrophobicity	Amount of Artifacts	Surface area (m ² /g)	Sorbent strength	Maximum Temperature (°C)	Applicable volatility range	Example of analytes
Porous organic polymers									
Tenax TA	Poly (2,6-diphenyl- <i>p</i> -phenylene oxide); Non-friable	Unreactive, good for labile analytes	Hydrophobic	< 1 ng	~35	Weak	350	Bp 100-400 °C; n-C ₇ to n-C ₃₆	All aromatics except benzene, non-polar compounds (bp > 100 °C) and semi-volatile polar compounds (bp > 150 °C).
Tenax GR	Poly (2,6-diphenyl- <i>p</i> -phenylene oxide) + 23% graphitized carbon; Non-friable	Unreactive, good for labile analytes	Hydrophobic	< 1 ng	~35	Weak	350	Bp 100-450 °C; n-C ₇ to n-C ₃₀	Alkylbenzenes, polycyclic aromatic hydrocarbons, polychlorobiphenyls and as above for Tenax TA. Replaced by Tenax TA for lower background interferences.
Chromosorb 102	Styrene-divinylbenzene co-polymer; Non-friable	Unreactive, good for labile analytes	Hydrophobic	~10-50 ng/component	~350	Medium	250	Bp 50-200 °C	Extensive spectrum of VOCs such as volatile oxygenated compounds, haloforms and chlorinated pesticides with bp > 40 °C (i.e. less volatile than dichloromethane)
Chromosorb 106	Polystyrene; Non-friable	Unreactive, good for labile analytes	Hydrophobic	~10-50 ng/component	~750	Medium	225-250	Bp 50-200 °C; n-C ₅ to n-C ₁₂	Low-boiling hydrocarbons, benzene, labile compounds, volatile oxygenated compounds.
Porapak N	Polyvinylpyrrolidone; Non-friable	Unreactive, good for labile analytes	Hydrophilic; dry-purging is required.	~10-50 ng/component	~300	Medium	190	Bp 50-200 °C; n-C ₅ to n-C ₈	Volatile nitriles (acrylonitrile, acetonitrile and propionitrile), pyridine, low-boiling alcohols, ethanol and 2-butanone.
Porapak Q	Ethylvinylbenzene-divinylbenzene co-polymer; Non-friable	Unreactive, good for labile analytes	Hydrophobic	~10-50 ng/component	~550	Medium	250	Bp 50-200 °C; n-C ₅ to n-C ₁₂	Wide range of VOCs such as oxygenated compounds, but unsuitable for amines, anilines and nitric oxides.
HayesSep D	Divinylbenzene polymer; Non-friable	Unreactive, good for labile analytes	Hydrophobic	~10-50 ng/component	~800	Medium	290	Bp 50°C-200°C; n-C ₅ to n-C ₁₂	GB/GE derivatives of VX (Chemical warfare agents), light compounds including acetylene, halogen-containing and sulfur-containing compounds, CO and CO ₂ .

Table 1.2: Physical and chemical characteristics of graphitized carbon blacks, zeolite molecular sieves and activated charcoal [33, 34, 79, 81, 86]. Bp stands for VOC boiling point.

Sorbent	Chemical Composition & friability	Chemical Inertness	Hydrophobicity	Amount of Artifacts	Surface area (m ² /g)	Sorbent strength	Maximum Temperature (°C)	Applicable volatility range	Example of analytes
Graphitized carbon blacks									
Carbotrap C/ Carbopack C/ Carbograph 2TD	Graphitization of the surface of carbon blacks. Different degree of graphitization would result in surface area variations. Friable and compressible, pack with care.	Contain trace amounts of metals, unsuitable for labile compounds such as thiols due to the activity of the material	Hydrophobic	< 0.1 ng	~12	Very weak	> 400	n-C ₈ to n-C ₂₀	Hydrocarbons to C ₂₀ , alkyl benzenes, heavy organics: polychlorobiphenyls, polynuclear aromatics
Carbotrap B/ Carbopack B/ Carbograph 1TD					~100	Medium-weak	> 400	n-C _{5/6} to n-C ₁₄	Wide range of VOCs including ketones, alcohols and aldehydes (bp > 75 °C), and all polar compounds within the volatility range specified, and perfluorocarbon tracer gases
Carbopack X					~240	Medium	> 400	n-C ₃ to n-C ₈	Low molecular mass hydrocarbons, benzene, toluene, ethylbenzene, xylene isomers, 1,3-butadiene.
Carbograph 5TD					~100	Medium	> 400	Bp 50 °C - 150 °C; n-C _{3/4} to n-C _{6/7}	Low molecular mass hydrocarbons between C ₃ to C ₈ , 1,3-butadiene
Zeolite molecular sieves									
Molecular sieve 5A	Non-friable	-	Significantly hydrophilic; usage is not advisable for humid conditions.	~10 ng	> 1200	Very strong	350-400	Bp (-60)-80 °C	Nitrous oxide and permanent gases
Molecular sieve 13X	Non-friable	-			> 1200	Very strong	350-400	Bp (-60)-80 °C	1,3-butadiene and permanent gases
Activated charcoal	Product of low-temperature oxidation of vegetable charcoal. Friable.	May catalyze the degradation of ketones	Tendency to retain water.	-	> 1000	Very strong	400	Bp (-60)-80 °C	Metal content may catalyze analyte degradation. Seldom used for thermal desorption. With care, ultra-volatile hydrocarbons. (C ₂ , C ₃ and C ₄)

Table 1.3: Physical and chemical characteristics of carbon molecular sieves [33, 34, 79, 81, 86]. Bp stands for VOC boiling point.

Sorbent	Chemical Composition & friability	Chemical Inertness	Hydrophobicity	Amount of Artifacts	Surface area (m ² /g)	Sorbent strength	Maximum Temperature (°C)	Applicable volatility range	Example of analytes	
Carbon molecular sieves										
Spherocharb/ Unicarb	Generated from the thermochemical decomposition of organic polymers such as poly(vinylchloride) or corresponding copolymers. Elimination of hydrogen chloride occurs at 180 °C and the remainder from the reaction is the porous carbon backbone. Non-friable.	Unreactive, good for labile compounds	Hydrophilic: dry-purging is required.	< 0.1 ng	~1200	Strong	> 400	Bp (-30)-150 °C; n-C ₃ to n-C ₈	Very volatile and small analytes (Vinyl chloride, ethylene oxide, carbon disulfide, dichloromethane, chloroform). Very volatile and spatially large molecules such as sulfur hexafluoride. Low-boiling polar compounds such as methanol, ethanol and acetone.	
			Significantly water-retentive – avoid usage in high humidity.		~800	Very strong	> 400	Bp (-60)-80 °C; Ethane to n-C ₅		
			Less hydrophilic compared to other carbon molecular sieves, dry-purging may still be needed.		~485	Strong	> 450	Bp (-30)-150 °C; n-C ₃ to n-C ₈		
Carboxen 569										Volatile hydrocarbons
Carboxen 1000						Prone to water retention – unsuitable for high humidity environments, dry-purge extensively prior to usage.	>1200	Very strong	> 400	Bp (-60)-80 °C; C ₂ to C ₃
Carboxen 1003			Hydrophilic: dry-purging may be necessary.		1000	Very strong	400	Ethane to n-C ₃	Ultra-light compounds such as C ₂ to C ₅ hydrocarbons, permanent gases such as H ₂ , O ₂ , Ar, CO, CO ₂	

for the sorbent to be hydrophobic to prevent the water vapor in the air from influencing analyte breakthrough. Dry purging has to be carried out stringently for hydrophilic sorbent materials such as Porapak N, UniCarb, Carboxens, Carbosieves and molecular sieves to minimize water retention on the material [78, 79].

Sorbent inertness is the measure of the material's reactivity with target VOCs. Graphitized carbon blacks such as Carbotrap C and Carbograph 1TD have trace amounts of chemically reactive species within them, such as trace metals and cannot be used for determining labile compounds such as thiols and monoterpenes [79]. The analysis of chemically reactive species has to be conducted using inert sorbent materials. Porous polymer sorbents are excellent for analyzing labile compounds.

Thermal stability varies between different sorbent materials. Carbon-based sorbents do not degrade as easily as most porous polymers and can be heated to temperatures higher than 400 °C [86]. Porous polymers such as Chromosorbs and Porapaks cannot be heated beyond 225 °C as they generally have lower thermal stability [80]. Tenax sorbents (Tenax TA and Tenax GR) are exceptional cases in the porous polymer family that have high thermal stability; both of which are stable at temperatures as high as 350 °C [78] .

The friability of the sorbent is the ease to which the sorbent grains are powdered into fine grains when compressive forces are acting on them. Graphitized carbon blacks are extremely vulnerable to mechanical force exerting on them, as it can alter the structure within the sorbent material and hence affect the adsorption/desorption properties of the sorbent. Proper precautions have to be taken when packing graphitized carbon blacks. Most of the other commercial sorbents available are non-friable.

Artifacts are compounds that are inherently generated by the sorbent material itself which could potentially interfere with the accuracies of trace quantitative analysis. The levels of artifacts present in different types of sorbent materials vary from one another. For instance, the levels of artifacts are lowest (< 0.1 ng) in graphitized carbon blacks and most in carbon molecular sieves [79]. The majority of the porous polymer sorbents, with an exception of Tenax (< 1 ng), have large amounts of artifacts ($=10$ ng) and cannot be used for the low-level quantification of certain compounds [86].

1.3.3 Active Sampling

The flow and volume of air into the sorbent tube is controlled by a calibrated pump in active sampling. Forced air of definite volume and flow enters the sorbent tube and the VOCs in the air are trapped by the sorbent materials in the tube. Diffusion of air into the stored sorbent tube is prevented by the usage of Difflok (diffusion-locking) caps. The principles behind diffusion locking are based on the width and the length of the inlet/outlet tube of a sampler. By narrowing the width and increasing the length, the diffusion of gases leaving or entering the tube can be reduced to near zero. The variability of air volume and flow for active sampling are conventionally between 0.1 to 150 litres and 10 to 1000 mL/min respectively [34, 81]. However, recent advancements in technology have allowed low flow active sampling between 0.5 to 1 mL/min with minimal or no influences from diffusion uptake. The sorbent is encased into a Safelok tube which has specially designed diffusion lock inserts in the air gaps at both ends of the tube [87, 88].

The optimum volume and flow have to be determined for the analytical application. While higher volumes would enhance the sensitivity of analytical methods, it could increase the risk

of breakthrough of analytes through the sorbent materials. Higher flow rates can also result in higher breakthrough values. Both trends were observed in Gallego et al. [76]. A comparative breakthrough investigation was conducted for a multi-sorbent tube consisting of Carbotrap, Carbopack X and Carboxen 569 and a single sorbent tube containing Tenax TA by varying the flow rates (70 mL/min and 90 mL/min for the collection of 90 L) and the volume of air collected (10 L, 20 L, 40 L, 60 L and 90 L sampled at 70 mL/min). The breakthrough values are calculated as percentages of VOC detected at the back tube when two similar tubes were connected in series with a calibrated pump attached at the back end. While the experiment confirmed that the multi-sorbent tube has a lower tendency of analyte leakages compared to the single sorbent tube, the experimental data also showed that increasing flows and volumes corresponded to higher percentage breakthrough.

Although information about certain VOC breakthrough and safe sampling volumes in various types of sorbent materials are available, there is much to be discovered and yet to be determined. First of all, there is a wide spectrum of VOCs with unknown breakthrough and safe sampling volumes in numerous different types of sorbents, yet to be verified. Secondly, when sorbent materials were used in combination, the breakthrough properties of the multi-sorbents are altered and have to be determined. Brown and Crump [89] carried out a study to compare the usefulness of a quartz wool/Tenax TA/Carbograph 5TD multi-sorbent tube and Tenax TA sorbent tube for sampling 21 VOCs and very volatile organic compounds (VVOCs) emitted from products that are used indoors. A Markes Micro-chamber/Thermal Extractor and a Field and Laboratory Emission Cell were used for the VOC emissions testing from two materials and air was actively sampled into the tubes using pumps. VVOCs experiments were performed by injection of VVOC mixtures into the inner surface of self-customized

Nalophan bags with their outlets attached to two Tenax TA or two multi-sorbent tubes that were connected in series. At the back end of the connected sorbent tubes a personal sampling pump was utilized for sampling at varying air volumes and flow rates. It was found that the safe sampling volume for the multi-sorbent tube was ≥ 10 L, whereas the safe sampling volume of Tenax TA tube falls between < 200 mL to 3.5 L.

Ribes and coworkers [32] developed a dynamic-sampling analytical procedure that incorporated isocyanates, isocyanato- and isothiocyanatocyclohexane as target compounds which was not done by any previous study. A multi-sorbent tube comprising of Carbotrap, Carbopack X and Carboxen 569 was employed for method optimization and validation. The breakthrough data obtained during active sampling (at 100 L and 135 L) and injection of standards (2000 ng) revealed that the multi-sorbent tube is suitable for determining all isocyanates, isocyanato- and isocyanatocyclohexane. In another study, Ramirez and colleagues established a method specifically for determining semi-VOCs emitted from 14 personal care products such as synthetic musks, parabens and insect repellants using Tenax TA tubes. It was mentioned in the literature [90] that the sampling volumes for indoor and outdoor determination of the compounds have to be lowered as parabens are more susceptible to breakthrough.

Recent publications on sorbent tube active sampling methods employ various types of multi-sorbent tubes to extend the spectrum of target VOCs (i.e. polarity and molecular mass) that can be analyzed. Ras-Mallorquí et al. [91] developed an analytical procedure for the determination of 54 gaseous VOCs using Tenax/Carbograph 1TD with recoveries that were higher than 98.9% for almost all analytes, and high precisions with percentage relative standard deviation (%RSD) obtained for all VOCs lower than 4%. The linearity coefficients

for calibration between 0.02 to 500 ng were ≥ 0.999 for all compounds and the method detection limits ranged from 0.01 and $1.25 \mu\text{g m}^{-3}$ for a sampling volume of 1200 mL. Kuntasal et al. [92] utilized Tenax TA/Carbopack B multi-sorbent tubes for evaluating 102 individual VOCs with average recoveries between 80 to 100% and the %RSD for repeatability all below 8%. The linearity of the calibration between 0.5 and 160 ng for all VOCs was above 0.99 and the range of method detection limits was 0.01 to 0.14 ppbv. Both studies implemented their methods for field studies in their respective locations. Ras-Mallorquí et al. used the procedure for monitoring outdoor gaseous pollutants in the urban and industrial areas in Tarragona, Spain whereas Kuntasal et al. utilized the method for different microenvironments: Gas stations, offices and residential households.

1.3.4 Passive Sampling

The mechanism of concentrating VOC analytes on sorbent beds in passive dosimetry is by diffusion of gaseous molecules from the exposed side of the sample tube. The net transport of VOC species being trapped onto the sorbent material coming from the outer sampling environment ceases when equilibrium is reached or discontinued by the user. Mathematically, the process which is also known as Fick's first law is described by the equation 1.2:

$$\frac{m}{(t \times A)} = \frac{D(C_a - C_f)}{L} \dots\dots\dots (1.2)$$

Where m is the diffused VOC mass (μg), t is the sampling duration (s), A is the cross-sectional area of the diffusion path (cm^2), D is the diffusion coefficient of the VOC (cm^2/s), C_a is the VOC concentration found in the air, C_f is the VOC concentration above the sorbent and L is the length of the diffusion path (cm). The equation can be simplified further based

on the assumption that the sorbent material behaves as an ideal sink. Thus, C_f is zero and the expression can be rearranged to become equation 1.3:

$$\frac{m}{(t \times C_a)} = \frac{D \times A}{L} \dots\dots\dots (1.3)$$

The term “ $\frac{m}{(t \times C_a)}$ ” is known as the diffusion uptake rate or infiltration rate. According to theory, this term should remain constant for a specific type of sampler and VOC with the condition that the VOC mass collected is continuously below the sorbent material’s retention capacity. Hence, the atmospheric VOC concentration could be calculated when the rate of diffusion uptake was evaluated.

There are two types of passive samplers, namely: axial and radial samplers. They can be differentiated by their geometrical dimensions. Axial samplers have smaller cross-sectional areas and longer diffusion pathways whereas radial samplers have larger cross-sectional areas and shorter diffusion lengths. Generally, the rate of diffusivity of axial samplers decreases to a constant level after some time of sampling due to the concentration gradient between the entrance to the diffusion region of the sampler and the surface for adsorption [93-95]. Radial samplers however, have greater rates of diffusivity than axial samplers because of the different direction of diffusion (i.e. radial diffusion) [96-98]. Figure 1.6 shows how axial and radial samplers function during the collection of samples.

The current literature reports indicate that there is interest in understanding more about the experimental diffusive uptake rates during sampling for both types of samplers, as compared to the theoretical values and those determined by commercial suppliers using exposure chambers. Walgraeve and colleagues explored the extent of deviation in experimental uptake

Figure 1.6: Axial and radial passive sampling.

rates to the ideal values in two publications [99, 100]. The uptake rate behavior for axial-type passive samplers (i.e. Tenax sorbent tubes) was studied under controlled temperature conditions at varying relative humidity for various diffusive exposure durations in both studies.

In the first report [99], 4 target compounds namely: limonene, toluene, ethyl acetate and hexane were investigated for the discrepancies in their theoretical rates of diffusivity. A power law relationship was established between the mass of VOC adsorbed and the concentration rate during exposure for all compounds of interest based on the experiments performed, with VOCs that were poorly adsorbed by Tenax exhibiting the greatest deviation of up to 50% from the predicted linear relationship. Thus, the theoretical infiltration rates are not recommended for calculations and instead it is proposed the utilization of internal standard calibration when conducting passive sampling.

Similar conclusions were drawn from the second study [100], in which the experimental uptake rates of 25 VOCs were investigated with active sampling being employed as a

reference sampling method and the relative ratios of real environments to theoretical uptake rates deviating by as much as a factor of 3. Other than the experimental uptake values being 1.4 to 3.8 times below the theoretical uptakes, infiltration rates that were determined under controlled laboratory conditions when exposed continuously to a single VOC were twice of the values obtained in real environments.

Another publication by Xian and coworkers [101] suggested an alternative approach for the experimental determination of diffusion uptake rates of more than 80 atmospheric VOCs. They devised a method that could also eliminate the necessity for accurate adjustment of pumps to low flow rates for active sampling by using reported uptake rates of reference VOCs and peak area ratios of samples obtained from passive and active sampling simultaneously at the same location. The procedure that was developed is versatile and could be implemented for all types of passive samplers but with the condition that the uptake rates of reference chemicals are verified.

Gallego et al. [102] evaluated the radial passive sampling in comparison to active sampling and found that there were significant differences in the majority of the concentrations obtained from the two different sampling procedures in spite of having comparable analytical characteristics during method validation. The concentrations measured using Radiello tubes were higher than pumped sampling. Hence, calculation of the real diffusion sampling rate is essential to prevent overestimation of the value that was determined by suppliers via exposure chambers.

Due to the distinct direction of diffusion in radial samplers as compared to axial samplers, sampling times could be a factor that affects the uptake rates. Gallego et al. [103]

investigated in another separate study how the duration of sampling and atmospheric VOC concentrations could influence the uptake performance of radial-type passive samplers. Radiello diffusive tubes with 4 replicates were sampled for different periods (3, 4, 7 and 14 days) during each sampling experiment. The results revealed that more than half of the measurements show significant differences between the total mass of VOCs collected in two short sampling intervals and in one equally long sampling period. Longer sampling durations introduces more uncertainties to the results as it can lead to back diffusion especially when weak sorbents were utilized for sampling.

Other meteorological factors that could also alter the uptake values are temperature and wind speed. Król et al. [104] performed statistical linear regression on the benzene concentrations measured from radial passive and on-line sampling. Poor correlation was observed and it was believed that variable uptake rates were the primary contribution to uncertainties in the data. The sampling uptakes were calculated for each interval of exposure by utilizing the monthly temperature mean. Plots of the daily temperature variations and the average temperature line demonstrated that the employment of the monthly temperature mean for calculations could result in considerable inaccuracies to the calculated uptake rates. Roukos and coworkers [105] discovered that there is a corresponding increment in the uptake rate of the passive sampler when the wind speed increases logarithmically. When the wind speed falls between 0.2 to 1.4 m/s, the enormity of that effect was found to be $\pm 13\%$.

1.4 New Trends in VOC Analysis using TD-GCMS

There are a few types of sorbent materials that have been developed in the recent years for VOC analysis using TD-GCMS. Wu et al. [106] reported the synthesis and the application of

mesoporous silica MCM-41. The material was tested for its potential as a sorbent by adsorption of known concentrations of standard mixtures into each material and comparing the calculated per carbon response of the flame ionization detector to that of other conventional sorbents or multi-sorbents. Although MCM-41 exhibits similar adsorption capabilities to the multi-sorbent carbons for VOCs between C8 to C12, poor retention of smaller VOCs between C3 to C7 was observed for the material. It was also noted that a much lower desorption temperature (i.e. 150 °C) is required to attain acceptable recovery values that carbon molecular sieves could only achieve at 300 °C. López and colleagues [64] assessed two poly(styrene-divinylbenzene) resins: Bond Elu ENV and LiChrolut EN that are commonly utilized in solid phase extraction for air sampling. Both materials were compared to Tenax TA as a reference and evaluated against 7 VOCs with elution curves plotted at two temperatures. Poor chromatographic elution was observed for LiChrolut EN in spite of having superior retention to both Bond Elu ENV and Tenax TA. Bond Elu ENV demonstrated the best chromatographic behavior and has a much lower theoretical plates than the other two materials. Both poly(styrene-divinylbenzene) resins have much faster retention decline with respect to temperature compared to Tenax TA.

New samplers and modified TD-GCMS techniques have also been established to improve analytical procedures for quantifying VOCs. Du and coworkers [107] inspected a new cost-effective passive sampler called Tsinghua Passive Diffusive Sampler (THPDS) coupled with hydrophobic silica zeolites as sorbents for the determination of indoor benzene, toluene and xylene isomers. In addition to the novel design of the sampler, this work has also extended the applications of zeolite materials for monitoring the mentioned aromatic compounds. The effects of wind speed on THPDS are minimal due to the porous cylinder acting as a diffusion

barrier during strong winds. Infiltration rates evaluated in exposure chambers with controlled conditions (wind speed and humidity) and known exposure doses of VOCs are relatively constant. Temperature was found to have negative impacts on the uptake measurements and corrections associated to temperature were implemented. Excellent correlation was observed when their performance was validated in real sampling environments with active sampling used as a reference method.

Recent derivatized TD-GCMS techniques were also evaluated for the determination of semi-VOCs and particle-phase molecular markers. The purpose of derivatization was to attain higher sensitivity (i.e. lower detection limits) which is mandatory for high temporal resolution data and at the same time, does not chemically affect the recoveries of non-polar moieties. In-situ methylation TD-GCMS was employed by Sheesley and coworkers [108] for analyzing secondary organic tracers from PM_{2.5} filters collected from motor vehicle emissions. Organic carbon loadings from two punches of the quartz filter were added with diazomethane after addition of internal standards and solvent evaporation to methylate the acid groups. The methylated filter sample was transferred into a glass tube for two-stage thermal desorption and GCMS analysis.

1.5 Atmospheric VOC Profiles in Different Countries

Based on VOC monitoring reports in recent years (2005 to 2013), canister sampling and gas chromatography are the most common sampling technique and analytical instrument used for VOC analysis. In addition to canisters, other sampling approaches that are employed include sorbent tubes, Tedlar bags and cartridges containing charcoal or dinitrophenylhydrazine (DNPH). It was noted that solvent free thermal desorption methods are now more widely

used as compared to the traditional carbon disulfide extraction. Acetonitrile extraction of VOCs from DNPH cartridges, followed by high performance liquid chromatography (HPLC) are utilized for the analysis of carbonyl compounds [58, 109, 110]. Both types of solvent extraction approaches are featured in the minority of the recent publications [110-116]. Growing interest in environmental pollution could be seen in China as several studies were carried out in Xiamen, Beijing, Guangzhou, Zhejiang, Foshan and Hong Kong over last two years [111, 112, 117-120]. As for developed nations such as United Kingdom, Switzerland and South Korea, transitions in analytical methods were observed for VOC screenings. Shifting from manual sampling methods, these countries now performed pollutant monitoring using online automated TD-GCMS equipment at fixed sampling intervals [121-124].

The most common VOC contaminants of interest are aromatics such as benzene, toluene, ethylbenzene and xylenes (collectively known as BTEX), non-methane hydrocarbons (NMHCs) from C2 to C12, carbonyl compounds and chlorofluorocarbons (CFCs). Some countries such as Spain have investigated the effects of halogenated VOCs in industrial sites [91, 116]. Table 1.4 shows the average concentrations of selected aromatic VOCs from different cities in 8 countries while Table 1.5 summarizes concentrations of the same compounds in Table 1.4 that were sampled and calculated based on seasonal variations in 3 different countries. The sampling locations, methodologies and seasons are summarized in both tables. The largest average concentrations of BTEX were observed in different cities in India [109, 114, 125, 126]. The highest benzene and toluene average were found at a petrol pumping station and at a traffic intersection situated in Mumbai at $540 \mu\text{g m}^{-3}$ and $303 \mu\text{g m}^{-3}$ respectively [126] .

The largest mean for ethylbenzene was registered during the daytime in New Alipore, Kolkata at $36 \mu\text{g m}^{-3}$, while the biggest *m,p*-xylene mean values was $90 \mu\text{g m}^{-3}$ collected at the All India Institute of Medical Sciences, New Delhi [109]. The minimum average concentrations of BTEX ($0.004 \mu\text{g m}^{-3}$ to $0.1 \mu\text{g m}^{-3}$), on the other hand were detected at the high alpine station situated in Jungfraujoch, Switzerland during the summer season [123].

Similar trends were noted for carbonyl compounds given in Tables 1.6 and 1.7. The biggest and smallest mean concentrations of C1 to C6 alkenals were from India and Switzerland respectively. The only exception is the value for pentanal ($1.7 \mu\text{g m}^{-3}$), which was measured at Lok Ma Chau, Hong Kong in summer [112]. Maximum average values for acetaldehyde ($18.9 \mu\text{g m}^{-3}$), propanal ($4.0 \mu\text{g m}^{-3}$), butanal ($5.2 \mu\text{g m}^{-3}$) and hexanal ($4.4 \mu\text{g m}^{-3}$) were found in New Alipore, Kolkata while the value for formaldehyde ($26.1 \mu\text{g m}^{-3}$) was observed in Shyambazar, Kolkata [109]. These maxima values were all seen during the daytime, implying that daylight plays an important role in enhancing the amounts of these carbonyl compounds. As for the minima values, they are all identified during autumn either in Jungfraujoch or Zurich. The lowest for formaldehyde ($0.4 \mu\text{g m}^{-3}$), acetaldehyde ($0.6 \mu\text{g m}^{-3}$), propanal ($0.05 \mu\text{g m}^{-3}$), pentanal ($0.02 \mu\text{g m}^{-3}$) and hexanal ($0.04 \mu\text{g m}^{-3}$) were all recorded at the high alpine monitoring station between Jungfrau and Monench, while butanal ($0.06 \mu\text{g m}^{-3}$) was registered in Kasernenhof [123].

Generally, China and South Korea have the highest reported levels for NMHCs while French rural areas have the lowest [119, 127-129]. Average concentrations of NMHCs are tabulated in Tables 1.8 to 1.11. Hydrocarbons that conform to the stated pattern are ethane, propane, isopentane, n-pentane, 2,4-dimethylpentane, 2,2,4-trimethylpentane, n-hexane, cyclohexane, 2-methylhexane, n-octane, ethene and propene. Other prominent NMHCs such as

Table 1.4: Average BTEX concentrations (in $\mu\text{g m}^{-3}$) around the world. “-” represents no data reported for that VOC.

Source	Country	Location	Sampling site/s	Method	Benzene	Toluene	Ethylbenzene	<i>m,p</i> -Xylene	<i>o</i> -Xylene
[117]	China	Haicang District, Xiamen	Southern Industrial area	Canister sampling, GCMS analysis	4.7	65.8	5.9	6.7	20.4
			Xinyang Industrial area		20.3	180	23.3	14.3	14.3
			Harbour and storage area		19.1	179	6.7	9.6	7.2
			Administration area		6.3	77.6	4.4	4.6	8.7
			Xinyang residential area		6.9	103	12.2	10.1	10.8
[118]	China	Guangzhou	Background site	Canister sampling, GCMS analysis	4.2	42.9	5.3	5.5	3.9
			Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Tianhe District of Guangzhou, South China		5.5	15.8	4.5	7.2	-
[119]	China	Foshan	Foshan Environmental Monitoring Station	Canister sampling, GCMS analysis	12.9	41.4	10.6	6.0	3.3
[129]	China	Hong Kong	Tap Mun	Canister sampling, GC/FID analysis	1.3	3.9	0.5	0.7	0.3
			Central/Western		1.3	10.4	1.7	3.1	1.0
			Tung Chung		1.5	8.5	1.5	2.1	0.7
			Yuen Long		2.3	16.4	2.4	4.0	1.3
[128]	South Korea	Seoul	Sung-su station	Online GCMS	2.7	150	18.9	22.8	9.0
[130]	India	Mumbai	Deonar	Sorbent-based sampling, GCMS Analysis	286	70.5	0.5	-	-
			Malad		145	87.1	0.2	-	-
			Residential		24.6	28.2	2.6	7.4	1.0
[125]	India	Delhi	Commercial	Canister sampling, GCMS analysis	417	115	28.8	48.7	-
			Industrial		208	47.2	30.1	16.1	0.5
			Traffic intersection		300	34.5	33.9	25.5	-
			Petrol pump		398	46.3	2.3	3.2	4.0

Table 1.4: Average BTEX concentrations (in $\mu\text{g m}^{-3}$) around the world. “-” represents no data reported for that VOC (continued).

Source	Country	Location	Sampling site/s	Method	Benzene	Toluene	Ethylbenzene	<i>m,p</i> -Xylene	<i>o</i> -Xylene
[126]	India	Mumbai	Residential	Sorbent-based sampling, TD-GCMS Analysis	45.3	29.2	0.2	-	0.3
			Commercial		127	129	0.3	-	0.2
			Industrial		202	79.6	0.3	-	0.08
			Traffic intersection		348	303	3.0	-	0.5
			Petrol pump		540	44.8	1.2	-	0.8
[114]	India	Delhi	Jawaharlal Nehru University	Carbon disulfide extraction from charcoal cartridge, GC/FID Analysis	48	85	7	30	15
			Connaught Place		97	180	21	83	40
			Okhla		89	204	16	61	41
			All India Institute of Medical Sciences		110	191	24	90	41
[109]	India	Kolkata	New Alipore (Day)	Active sampling with DNPH cartridge followed by solvent extraction, HPLC Analysis	63.7	73.2	36.3	34.5	11.0
			New Alipore (Night)		42.8	41.6	15.0	19.0	8.1
			Gariahat (Day)		33.6	41.4	11.0	15.7	12.5
			Gariahat (Night)		25.0	27.7	4.5	11.2	8.1
			Shyambazar (Day)		79.2	86.2	16.4	29.6	22.6
[127]	France	Donon, Peyrusse-Vieille and Tardiere	Shyambazar (Night)	Canister sampling, GC/FID analysis	78.8	103	20.2	35.9	14.7
			Donon		0.5	0.6	0.1	0.3	0.1
			Peyrusse-Vieille		0.4	0.4	0.08	0.2	0.1
[131]	Turkey	Kocaeli	Tardiere	Sorbent-based passive sampling, TD-GCMS Analysis	0.5	1.0	0.2	0.6	0.2
			Middle East Technical University, Environmental Engineering Department		2.3	35.5	9.7	36.9	12.5
[122]	United Kingdom	London	Marylebone Road Kerbside	Online TD-GCMS	-	21.7	4.0	13.9	5.1
[58]	Japan	Tokyo	Urban 2003	Canister sampling, GCMS analysis	2.5	21	4.1	5.2	1.9
			Roadside 2003		4.6	29	5.7	9.8	3.7
			Urban 2004		4	26	4.9	7.2	2.7
			Roadside 2004		2.3	19	3.9	4.6	1.7
[116]	Spain	Catalonia	Tarragona Site 1	Sorbent-based active sampling, TD-GCMS Analysis	1.5	2.6	1.9	1.2	1.0
			Tarragona Site 2		1.4	4.3	1.9	1.1	0.8
			Tarragona Site 3		0.5	1.1	0.5	0.5	0.4

Table 1.5: Average BTEX concentrations (in $\mu\text{g m}^{-3}$) around the world with seasonal variations.

Source	Country	Location	Seasons	Sampling site/s	Method	Benzene	Toluene	Ethylbenzene	<i>m-p</i> -Xylene	<i>o</i> -Xylene
[111]	China	Beijing	Autumn 2009	Research Centre for Eco-Environmental Sciences , Beijing	Sorbent-based active sampling- Gas Chromatography Photo Ionization Detector (GCPIID)	5.1	11.2	4.1	7.2	2.8
			Winter 2009			9.2	14.5	4.4	7.5	3.5
			Spring 2009			4.8	9.4	2.7	4.3	1.8
			Summer 2009			3.2	8.6	3.3	4.6	1.9
			Spring 2005			0.08	0.3	0.08	0.3	0.03
[123]	Switzerland	Jungfrauoch	Summer 2005	High alpine station Jungfrauoch	Online TD-GCMS	0.06	0.1	0.009	0.01	0.004
			Fall 2005			0.07	0.2	0.009	0.03	0.01
			Winter 2005			0.4	0.3	0.04	0.09	0.03
			Spring 2005			1.3	5.5	1.1	3.1	1.1
			Summer 2005			0.7	5.4	0.9	2.5	1.1
[124]	Switzerland	Zurich	Fall 2005	Kasementhof, Zurich	Online TD-GCMS	1.5	6.4	1.1	3.5	1.3
			Winter 2005/2006			2.4	4.7	0.9	2.9	1.1
			Summer			0.48	4.3	0.9	1.0	0.4
[115]	Japan	Shizuoka	Winter	Shimizu	Active sampling with charcoal cartridge, carbon disulfide extraction GCMS analysis	0.95	6.4	1.6	1.5	0.6

Table 1.5: Average BTEX concentrations (in $\mu\text{g m}^{-3}$) around the world with seasonal variations (continued).

Source	Country	Location	Seasons	Sampling site/s	Method	Benzene	Toluene	Ethylbenzene	<i>m-p</i> -Xylene	<i>o</i> -Xylene
[120]	China	Zhejiang, Fujian and Guangdong	Winter	Lucheng, Wenzhou	Tedlar Bag sampling, GC/MS analysis	10.8	96.9	4.3	4.8	3.6
				Jiaocheng/Ningde		5.3	16.3	1.6	2.2	1.6
				Jin'an/Fuzhou		8.5	23.8	2.3	3.1	2.2
				Fuqing/Fuzhou		6.2	14.2	1.4	1.6	1.2
				Dehua/Quanzhou		10.5	27.9	2.8	4.0	2.8
				Pingtian/Fuzhou		8.2	19.4	2.7	3.9	2.9
				Licheng/Putian		8.1	75.1	2.4	2.7	1.9
				Xiuyu/Putian		6.8	38.2	2.1	2.5	1.8
				Fengze/ Quanzhou		6.3	11.9	1.7	2.4	1.8
				Shishi/Quanzhou		3.8	9.7	1.2	1.4	0.9
				Jimei/Xiamen		22.5	37.1	2.0	2.6	2.0
				Longwen/Zhangzhou		11.4	37.6	5.2	5.6	4.0
				Siming/Xiamen		21.2	115	13.9	85.4	58.7
				Longhu/Shantou		12.2	46.9	3.6	3.9	2.8
			Summer	Lucheng, Wenzhou		6.4	37.7	3.1	3.1	2.2
				Jiaocheng/Ningde		1.7	12.5	0.7	0.7	0.4
				Jin'an/Fuzhou		1.9	6.1	0.8	0.8	0.5
				Fuqing/Fuzhou		2.7	8.5	1.1	1.1	0.7
				Dehua/Quanzhou		3.5	26.4	2.0	2.0	1.3
				Pingtian/Fuzhou		1.5	14.2	1.2	0.9	0.9
				Licheng/Putian		1.2	4.2	0.6	0.2	0.4
				Xiuyu/Putian		1.5	9.4	0.7	0.7	0.6
				Fengze/ Quanzhou		2.1	11.2	1.0	1.0	0.6
				Shishi/Quanzhou		3.6	15.8	1.7	1.7	1.1
				Jimei/Xiamen		4.3	50.4	1.5	1.5	1.3
				Longwen/Zhangzhou		2.0	5.6	0.8	0.8	0.6
				Siming/Xiamen		2.9	7.6	0.8	0.8	0.6
				Longhu/Shantou		2.6	17.7	2.2	2.2	1.4

Table 1.6: Average carbonyl concentrations (in $\mu\text{g m}^{-3}$) around the world. “-” represents no data reported for that VOC.

Source	Country	Location	Sampling site/s	Method	Formaldehyde	Acetaldehyde	Propanal	Butanal	3-Methyl butanal	Pentanal	Hexanal	Benzaldehyde
[110]	South Korea	Gumi National Industrial Complex	4th Industrial site	Active sampling with DNPH cartridge, solvent extraction, HPLC analysis	4.2	13.2	1.9	1.0	-	-	-	-
			5th Industrial site		4.8	4.5	2.4	0.8	-	-	-	-
			6th Industrial site		4.7	7.6	2.5	0.7	-	-	-	-
			Commercial site		4.1	3.7	2.5	0.8	-	-	-	-
			Residential site		4.3	4.2	2.9	0.7	-	-	-	-
[109]	India	Kolkata	New Alipore (Day)	Active sampling with DNPH cartridge, solvent extraction, HPLC analysis	23.9	18.7	4.0	5.2	2.3	1.4	4.4	3.4
			New Alipore (Night)		19.4	14.2	3.2	3.3	2.2	1.5	2.9	1.9
			Gariahat (Day)		14.0	9.5	2.1	3.9	1.8	0.7	1.0	3.0
			Gariahat (Night)		14.1	7.6	1.5	4.0	0.8	0.8	1.1	1.0
			Shyambazar (Day)		26.1	16.5	3.3	4.9	2.6	1.3	2.0	4.7
[58]	Japan	Tokyo	Shyambazar (Night)	Canister sampling; GC/MS analysis	22.4	12.3	2.4	3.6	1.5	1.0	2.9	3.3
			Urban 2003		3.1	3.3	-	-	-	-	-	-
			Roadside 2003		5.0	4.2	-	-	-	-	-	-
			Urban 2004		5.6	7.3	-	-	-	-	-	-
			Roadside 2004		4.8	5.2	-	-	-	-	-	-

Table 1.7: Average carbonyl concentrations (in $\mu\text{g m}^{-3}$) around the world with seasonal variations. “-” represents no data reported for that VOC while “n.d.” represents not detected.

Source	Country	Location	Seasons	Sampling site/s	Method	Formaldehyde	Acetaldehyde	Propanal	Butanal	3-Methyl butanal	Pentanal	Hexanal	Benzaldehyde
[111]	China	Beijing	Autumn	Research Centre for Eco-Environmental Sciences, Beijing	Active sampling with DNPH cartridge, solvent extraction, HPLC analysis	8.3	9.8	-	-	-	-	-	-
			Winter			4.3	5.3	-	-	-	-	-	-
			Spring			5.3	6.8	-	-	-	-	-	-
			Summer			8.8	9.5	-	-	-	-	-	-
[112]	China	Hong Kong	Summer	Lok Ma Chau	Active sampling with DNPH cartridge, solvent extraction, HPLC Analysis	25.2	5.4	1	-	0.7	1.7	0.7	0.5
			Winter			18.5	7.2	0.8	-	1.1	0.6	0.4	0.6
			Summer	Mong Kok		23.7	5.1	0.9	-	0.7	0.6	1.0	0.5
			Winter			17.1	6	0.7	-	1.6	0.7	0.6	1.0
			Summer	Hong Kong Polytechnic University		22.1	3.9	0.7	-	0.4	0.3	0.6	0.6
			Winter			13.3	6.1	0.5	-	0.8	0.4	0.5	0.8
[123]	Switzerland	Jungfraujoeh	Spring	High alpine station Jungfraujoeh	Online TD-GCMS	0.5	n.d.	n.d.	n.d.	-	n.d.	n.d.	0.04
			Summer			0.6	0.7	0.06	0.06	-	0.04	0.05	0.02
			Fall			0.4	0.6	0.05	0.07	-	0.02	0.04	0.03
			Winter			0.4	n.d.	n.d.	n.d.	-	n.d.	n.d.	0.02
[124]	Switzerland	Zurich	Spring	Kasernenhof, Zurich	Online TD-GCMS	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	n.d.
			Summer			2.9	1.4	0.3	0.2	-	0.1	0.3	0.09
			Fall			n.d.	0.8	0.3	0.06	-	0.07	0.1	0.04
			Winter			2.3	1.5	0.3	0.1	-	0.07	0.08	0.09
[115]	Japan	Shizouka	Summer	Shimizu	Active sampling with DNPH cartridge, solvent extraction, HPLC Analysis	2.3	2.8	0.4	0.2	0.09	0.1	0.6	0.3
			Winter			1.9	3.3	0.5	0.1	0.03	0.08	0.2	0.5

Table 1.8: Average alkane concentrations (in $\mu\text{g m}^{-3}$) around the world. “-” represents no data reported for that VOC.

Source	Country	Location	Sampling site/s	Method	Ethane	Propane	i-Butane	n-Butane	i-Pentane	n-Pentane	2,4-Dimethyl pentane	2,2,4-Trimethyl pentane	n-Hexane	Cyclo hexane	2-Methyl hexane	n-Heptane	n-Octane
[117]	China	Haicang District, Xiamen	Southern Industrial area	Canister sampling, GCMS analysis	-	-	-	-	-	-	-	-	4.0	-	-	1.3	-
			Xinyang Industrial area		-	-	-	-	-	-	-	-	23.2	-	-	25.7	-
			Harbour and storage area		-	-	-	-	-	-	-	-	26.8	-	-	5.7	-
			Administration area		-	-	-	-	-	-	-	-	6.6	-	-	1.1	-
			Xinyang residential area		-	-	-	-	-	-	-	-	9.1	-	-	4.3	-
			Background site		-	-	-	-	-	-	-	-	8.0	-	-	1.7	-
[129]	China	Beijing	Tsinghua University	Canister sampling, GCMS analysis	2.8	9.8	5.9	8.3	12.0	11.3	0.8	0.7	18.0	0.8	1.2	1.7	3.6
[118]	China	Guangzhou	Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Tianhe District, Guangzhou	Canister sampling, GCMS analysis	3.9	8.1	3.2	6.0	5.3	3.5	-	-	-	-	-	-	-
[119]	China	Foshan	Foshan Environmental Monitoring Station	Canister sampling, GCMS analysis	22.8	23.4	7.2	8.9	38.6	3.3	1.2	4.4	9.0	2.3	2.0	4.4	6.1

Table 1.8: Average alkane concentrations (in $\mu\text{g m}^{-3}$) around the world. “-” represents no data reported for that VOC (continued).

Source	Country	Location	Sampling site/s	Method	Ethane	Propane	i-Butane	n-Butane	i-Pentane	n-Pentane	2,4-Dimethyl pentane	2,2,4-Trimethyl pentane	n-Hexane	Cyclohexane	2-Methyl hexane	n-Heptane	n-Octane
[132]	China	Hong Kong	Tap Mun	Canister sampling, GC/FID analysis	2.2	1.6	0.8	1.4	1.1	0.5	-	-	-	-	-	-	-
			Central/Western		2.3	2.9	2.1	3.5	1.5	0.7	-	-	-	-	-	-	-
			Tung Chung		2.1	2.2	1.2	2.3	1.3	0.7	-	-	-	-	-	-	-
			Yuen Long		2.6	4.6	3.5	6.2	3.4	1.6	-	-	-	-	-	-	-
[128]	South Korea	Seoul	Sung-su station	Online GC/MS	4.7	17.3	7.5	12.8	6.6	3.5	28.6	2.1	11.6	5.4	1.8	2.5	1.5
[127]	France	Donon, Peyrusse-Vieille and Tardiere	Donon	Canister sampling, GC/FID analysis	2.1	1.2	-	0.9	0.6	0.3	0.03	0.07	0.1	0.07	0.06	0.07	0.07
			Peyrusse-Vieille		1.9	1.0	-	0.5	0.4	0.2	0.02	0.06	0.09	0.05	0.03	0.06	0.07
			Tardiere		2.2	1.3	-	0.7	0.6	0.5	0.02	0.1	0.1	0.07	0.05	0.08	0.09
[122]	United Kingdom	London	Marylebone Road Kerbside	Online TD-GC/MS	-	-	-	-	-	-	-	-	2.2	-	-	1.4	-
[58]	Japan	Tokyo	Urban 2003	Canister sampling, GC/MS analysis	-	-	7.1	1.3	7.2	4.6	0.2	0.3	2.5	0.9	0.7	0.8	0.3
			Roadside 2003		-	-	9.6	18.0	14.0	7.4	0.4	0.8	3.9	1.0	1.4	1.4	0.5
			Urban 2004		-	-	9.4	16.0	18.0	7.8	0.4	0.9	4.3	1.2	1.5	1.5	0.5
			Roadside 2004		-	-	7.0	12.0	9.5	4.4	0.2	0.4	3.0	1.0	0.8	1.0	0.4
[116]	Spain	Catalonia	Tarragona Site 1	Sorbent-based active sampling, TD-GC/MS analysis	-	-	-	-	-	2.1	-	-	1.1	-	-	-	-
			Tarragona Site 2		-	-	-	-	-	1.7	-	-	0.4	-	-	-	-
			Tarragona Site 3		-	-	-	-	-	0.9	-	-	0.3	-	-	-	-

Table 1.9: Average alkane concentrations (in $\mu\text{g m}^{-3}$) around the world with seasonal variations. “-” represents no data reported for that VOC while “n.d.” represents not detected.

Source	Country	Location	Seasons	Sampling site/s	Method	n-Butane	n-Hexane	n-Heptane
[120]	China	Zhejiang, Fujian and Guangdong	Winter	Luoheng, Wenzhou	Tedlar Bag sampling, GCMS analysis	-	13.0	2.6
				Jiaocheng/Ningde		-	6.2	1.2
				Jin'an/Fuzhou		-	7.7	1.8
				Fuqing/Fuzhou		-	7.1	1.2
				Dehua/Quanzhou		-	11.4	4.7
				Pingtan/Fuzhou		-	15.1	1.3
				Licheng/Putian		-	13.1	2.2
				Xiuyu/Putian		-	26.6	1.5
				Fengze/Quanzhou		-	6.6	1.2
				Shishi/Quanzhou		-	6.1	0.7
			Summer	Jimei/Xiamen		-	3.2	1.8
				Longwen/Zhangzhou		-	15.2	2.7
				Siming/Xiamen		-	65.9	5.5
				Longhu/Shantou		-	18.2	2.7
				Luoheng, Wenzhou		-	24.1	1.2
				Jiaocheng/Ningde		-	9.7	0.4
				Jin'an/Fuzhou		-	8.0	0.3
				Fuqing/Fuzhou		-	37.8	0.8
				Dehua/Quanzhou		-	17.4	1.0
				Pingtan/Fuzhou		-	14	n.d.
				Licheng/Putian		-	9.7	0.4
				Xiuyu/Putian		-	9.1	0.2
				Fengze/Quanzhou		-	11.3	0.6
				Shishi/Quanzhou		-	19.1	0.8
				Jimei/Xiamen		-	23.8	1.5
				Longwen/Zhangzhou		-	13.2	0.5
				Siming/Xiamen		-	12.3	0.4
				Longhu/Shantou		-	10.9	0.7

Table 1.9: Average alkane concentrations (in $\mu\text{g m}^{-3}$) around the world with seasonal variations. “-” represents no data reported for that VOC while “n.d.” represents not detected (continued).

Source	Country	Location	Seasons	Sampling site/s	Method	n-Butane	n-Hexane	n-Heptane
[123]	Switzerland	Jungfraujoch	Spring	High alpine station Jungfraujoch	Online TD-GCMS	0.1	-	-
			Summer			0.07	-	-
			Fall			0.1	-	-
			Winter			0.5	-	-
[124]	Switzerland	Zurich	Spring	Kasernenhof, Zurich	Online TD-GCMS	2.5	-	-
			Summer			1.6	-	-
			Fall			3.5	-	-
			Winter			2.9	-	-

Table 1.10: Average alkene concentrations ($\mu\text{g m}^{-3}$) around the world. “-” represents no data reported for that VOC.

Source	Country	Location	Sampling site/s	Method	Ethene	Propene	1-Butene	cis-2-Butene	trans-2-Butene	cis-2-Pentene	trans-2-Pentene	1-Hexene	1,3-Butadiene	Isoprene
[118]	China	Guangzhou	Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Tianhe District, Guangzhou	Canister sampling, GCMS analysis	3.2	3.9	-	-	-	-	-	-	-	1.8
[119]	China	Foshan	Foshan Environmental Monitoring Station	Canister sampling, GCMS analysis	23.6	11.8	4.4	1.1	1.4	0.8	0.8	1.6	-	1.0
[132]	China	Hong Kong	Tap Mun	Canister sampling, GC/FID analysis	1.0	0.2	0.1	-	-	-	-	-	0.04	0.9
			Central/Western		1.7	0.5	0.2	-	-	-	-	-	0.1	0.5
			Tung Chung		1.5	0.4	0.2	-	-	-	-	-	0.08	0.4
			Yuen Long		3.1	1.0	0.4	-	-	-	-	-	0.2	0.5
[128]	South Korea	Seoul	Sung-su station	Online GCMS	2.0	3.7	0.5	0.5	0.8	0.3	0.5	0.2	-	1.0
[127]	France	Donon, Peyrusse-Vieille and Tardiere	Donon	Canister sampling, GC/FID analysis	0.8	0.2	0.08	0.03	0.04	0.02	0.02	0.03	0.02	1.1
			Peyrusse-Vieille		0.5	0.2	0.05	0.01	0.01	0.01	0.01	0.03	0.02	1.4
			Tardiere		0.8	0.3	0.07	0.02	0.02	0.02	0.01	0.03	0.03	0.4
					-	-	1.3	1.0	1.2	0.7	1.3	-	-	-
[122]	United Kingdom	London	Marylebone Road Kerbside	Online TD-GCMS	-	-	2.3	0.6	0.7	0.2	0.4	-	0.3	0.4
[58]	Japan	Tokyo	Urban 2003	Canister sampling, GCMS analysis	-	5.3	2.3	0.6	0.7	0.2	0.4	-	0.3	0.4
			Roadside 2003		-	7.7	5.1	1.5	1.7	0.7	1.2	-	0.9	0.7
			Urban 2004		-	4.7	4.5	1.6	1.9	0.8	1.4	-	0.7	0.9
			Roadside 2004		-	3.6	2.3	0.6	0.7	0.3	0.5	-	0.3	0.5

Table 1.11: Average alkene concentrations (in $\mu\text{g m}^{-3}$) in Switzerland with seasonal variations. “-” represents no data reported for that VOC.

Source	Country	Location	Seasons	Sampling site/s	Method	Ethene	Propene	1-Butene	cis-2-Butene	trans-2-Butene	cis-2-Pentene	trans-2-Pentene	1-Hexene	1,3-Butadiene	Isoprene
[123]	Switzerland	Jungfraujoeh	Spring	High alpine station Jungfraujoeh	Online TD-GCMS	-	-	-	-	-	-	-	-	0.004	0.003
			Summer			-	-	-	-	-	-	-	-	0.002	0.1
			Fall			-	-	-	-	-	-	-	-	0.004	0.04
			Winter			-	-	-	-	-	-	-	-	0.004	0.01
[124]	Switzerland	Zurich	Spring	Kasernenhof, Zurich	Online TD-GCMS	-	-	-	-	-	-	-	-	0.2	0.2
			Summer			-	-	-	-	-	-	-	-	0.2	0.5
			Fall			-	-	-	-	-	-	-	-	0.2	0.2
			Winter			-	-	-	-	-	-	-	-	0.2	0.2

3-methylpentane, 1-butene, cis-2-butene, trans-2-butene, cis-2-pentene, trans-2-pentene have the largest means recorded in Tokyo and minimum values in Donon and Peyrusse-Vieille [58, 127]. Sources of NMHCs are anthropogenic and it is no surprise that developing nations like China and urbanized cities such as Seoul and Tokyo have higher levels of NMHCs that are usually found in vehicular fuels or from various industrial complexes. With low numbers of vehicles and industries in rural areas, NMHCs were expected to be much lower than in such places.

General seasonal variations were also observed for VOCs. Concentrations were generally lower in summer as compared to winter. This was noticed in several studies carried out in Beijing, Southeast China, Hong Kong, Jungfraujoch, Zurich and Shizuoka [111, 112, 115, 120, 123, 124]. Tong et al. [120] suggested that meteorological conditions have strong influences in VOC concentrations during different seasons. Higher VOC washouts were observed in summer due to higher occurrences of precipitation in summer as compared to winter. Other than rain, the monsoon winds and intensity of light could also favor or disfavor the removal of VOCs. Legreid and colleagues [123] proposed an explanation to the trend. Increased VOC mixing ratios in winter is due to lower mixing ratios of OH radicals ($\text{OH}^{\bullet}$) in winter. The dominant VOC sink mechanism is managed by this radical. Low $\text{OH}^{\bullet}$ result in longer life spans of other VOCs during winter. Some compounds however, exhibit an opposite behavior. Ho and coworkers [112] noticed that the total carbonyl concentrations were higher in summer than in winter. Secondary photochemical reactions are major sources for carbonyl compounds such as formaldehyde in summer where their concentrations are much greater. The study by Ho et al. also revealed that there are exceptional carbonyls such as acetaldehyde and benzaldehyde that have higher amounts during winter compared to summer and are accounted for by same postulations provided by Legreid and coworkers [112, 123].

1.6 Scope of Work

Air pollution has been an on-going problem that needs to be resolved. The key to resolving the issue lies in comprehending the mechanism of emissions and removal of pollutants by the natural environment and anthropogenic activities. Quantitative and qualitative information are imperative and essential for understanding the environmental cycles of pollutants. Recent technological advancements for monitoring VOCs and research featuring various sampling techniques and solvent-free analysis are described. In addition, new trends in VOC research and a summary of VOC profiles around the world from recent years are included. Prior to the selection of the appropriate analytical method, the user has to know the advantages and limitations of available techniques, the identity of VOC analytes that the user is interested in monitoring and whether the analytical method is compatible for the compounds of interest. As for the development and designing of novel techniques for improved quantification accuracy and sensitivity, fundamentals of the commercially available systems are important starting points for the expansion of new technology.

In Singapore, the amounts of atmospheric volatile organic pollutants present have not been previously studied nor reported by government authorities despite being recognized as one of the major constituent of air pollution. The key public organization in monitoring air quality island-wide, the NEA, reports the PSI calculated using the concentrations of 5 criteria gaseous contaminants (PM_{10} , SO_2 , CO, tropospheric O_3 and NO_x), their individual concentrations, as well as the amounts of $\text{PM}_{2.5}$ present [133, 134]. Atmospheric investigations performed in Singapore have focused mainly on comprehending the local environment during transboundary haze pollution caused by burning forests in nearby countries. Singapore suffers serious air quality problems annually from such smoke events caused by biomass burning. The primary interest of this study was to determine the

severity of VOC pollution in the western part of the country, home to the principal industrial estate in Singapore and one of the largest petroleum refineries in the world.

In order to study the composition of atmospheric volatile organic pollutants found in the western industrial zone in Singapore, an analytical procedure using TD-GCMS have to be established for the local conditions. Tenax/Carbopack X multi-sorbent tubes are employed for active sampling with calibrated pumps. Qualitative identification of gaseous organic species initially have to be performed by analyzing air samples collected in large volumes to ensure that the intensities of VOC signals in the chromatograms are sufficiently high. After matching unknown mass spectrums with known compounds from the National Institute of Standards and Technology (NIST) library database, a list of identified VOCs is compiled and their standards are purchased. The confirmation of the VOC identities is then carried out by analyzing the standards individually, matching their retention times (t_R) and relative abundances of representative and molecular ions with respect to the base ion.

Once their identities are confirmed qualitatively, the target analytes' standard mixture is prepared and the column separation of the analytes standard mixture is optimized by modifying the GC oven temperature program. The TD parameters are optimized next to minimize VOC analyte loss during the desorption processes. This is carried out after optimum VOC separation is attained. Analytical characteristics of the optimized method such as linearity, repeatability and sensitivity are validated. The performance of the sorbent tube during sampling, such as breakthrough, method detection limits and reproducibility of pumps also require investigation. When all validation and performance evaluation criteria are met, the procedure could be applied for environmental monitoring of those atmospheric organic contaminants.

Samples collected by the established procedure could be quantified and the concentrations for each VOC could be statistically analyzed. Daily trend profiles are employed for estimating the contribution of anthropogenic and biogenic sources, whereas Spearman correlations and coefficients of determinations could be utilized to investigate the pairs of compounds that shared mutually common or exclusive sources. Positive matrix factorization (PMF) modeling can be used to calculate the source profiles and VOC contributions from each source. To understand the effects of special events, such as the transboundary haze, on concentrations of certain organic analytes, monthly box plot analysis is used to evaluate the VOCs that are found in the Southeast Asian Haze, based on concentration spikes in the month of that event. The non-carcinogenic and carcinogenic hazards of harmful VOCs could be assessed by calculating hazard ratios (HR_i) and lifetime cancer risks (LCR_i), which allow an estimation of the health risks due to exposure of concentrations detected from the samples.

There are several drawbacks in using conventional TD sorbent materials such as Tenax and Carbopack X. They have limited thermal cycles and have to be replaced when their lifespan is up. These sorbents produce artifacts, compounds which are generated inherently from the material itself [91, 135-137]. Benzene and toluene are usually VOCs of importance due to their toxicity and are often target analytes for measurements. However, they are also artifacts commonly present in traditional sorbents that can interfere with the accurate determination of trace amounts found in the atmosphere. There has been a large increase in the use of carbon nanostructures in the field of analytical research. These nanomaterials have been evaluated expansively as potential sorbents in many analytical applications, due to their extraordinary physical and electronic properties. The feasibility of using different types of carbon nanotubes as sorbents for atmospheric sampling purposes first requires that their thermal stabilities during high temperature

heating is established using thermogravimetric analysis (TGA). CNTs are thus packed in a similar way as traditional sorbent materials in a sorbent tube. They are conditioned for removal of organic contaminants that can interfere with the analytes that are introduced into them during sampling experiments. The optimized conditioning parameters have to be evaluated by TGA to ensure that no thermal decomposition occurs during conditioning and analysis. CNT blanks also need to be analyzed for the presence of any artifacts and the artifacts quantified. A specified amount of VOCs that are identified and detected in ambient air in Singapore are loaded into the conventional sorbent tube (containing Tenax/Carbopack X) and CNT sorbent tubes. Comparisons of the desorption recoveries of VOCs between nanomaterials and the conventional sorbent materials are made. The effects of chemical functionalization and length of the CNTs on the analyte desorption recoveries could be evaluated by packing functionalized CNTs and shorter length CNTs into separate stainless steel tubes and comparing them with their non-functionalized and longer length counterparts. Raman spectroscopy can be implemented to evaluate the presence of defects in these nano sorbents, which provides information on the structural order found in the sorbent. The presence of defective sites in the material can be used to explain the desorption profiles obtain for certain VOCs. Microwave digestions coupled with inductively coupled plasma mass spectrometry (ICPMS) is utilized to investigate the metallic impurities in CNTs, which may play important roles in influencing the recoveries of some organic compounds of interest.

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Development of a Quantitative Assessment Method for Atmospheric Volatile Organic Pollutants using Thermal Desorption Gas Chromatography Mass Spectrometry

2.1 Introduction

Anthropogenic VOC emissions to the atmosphere can become conceivably harmful to all living organisms due to the continuous global industrial activities. The quantification of VOCs present in ambient air is therefore very important for developing regulations needed to control pollution. Environmental and health effects of some of these contaminants have been established in a number of previous investigations [1-4]. Halogenated VOCs (eg. tetrachloromethane and 1,1,1-trichloroethane) and chlorofluorocarbons (eg. CFC-11, CFC-12 and CFC-113) are precursors to stratospheric O₃ depletion [5, 6]. Photochemical smog is caused by reactions of NO_x and tropospheric O₃ together with VOCs such as NMHCs [7, 8]. Acute exposure to VOCs can induce irritation of mucous membranes, nausea, increase the risk of asthma and affect the nervous, immune and reproductive systems [9-11]. Chronic exposure to carcinogenic and mutagenic organic species can lead to cancer [12].

TD-GCMS is a solvent-free analytical technique that has become widely recognized and utilized for studying outdoor environmental pollution, indoor air quality and organic gases in different types of microenvironments. Applications of the analytical technique have been expanded further in recent years. For example, several toxic organic compounds

were incorporated as target analytes that were not previously analyzed. Terzic and coworkers optimized and validated a sensitive TD-GCMS procedure for screening trace amounts of chemical warfare agents and their impurities present in air samples [13]. Limits of detection between 0.8 to 2.9 ng were achieved for targeted nerve and blister agents such as o-isopropyl methylphosphonofluoridate and 2-chlorovinyl dichloroarsine. Andersen and colleagues [14] discovered the optimum analytical and storage conditions for sampling and determining methanethiol, a highly volatile and reactive organic compound via TD-GCMS. Ribes and coworkers [15] included isocyanates, isocyanato- and isothiocyanatocyclohexane as compounds of interest for detection in the atmosphere. Rodríguez-Navas et al. [16] reported another methodical approach for identifying and evaluating concentrations of 93 VOCs emitted collectively from municipal solid waste treatment plants.

Determination of safe sampling and breakthrough volumes of different types of multi-sorbent tubes for an extensive range of organic contaminants were also carried out in recent studies. This is because commercial suppliers of sorbent materials provide breakthrough information of limited types of VOCs which are only applicable to single sorbents. Detournay and colleagues evaluated the breakthrough of Carboxen 1000 and Carboxen 1000/Carbopack B multi-sorbent tubes at a flow of 200 mL/min for 6 aldehydes between C6 to C11, 8 hydrocarbons from C9 to C16, 6 monoterpenes and 5 aromatic compounds. They found that no analyte leakages were observed for sampling volumes as high as 120 L at ambient temperature, with a relative humidity of 75% [17]. Ramirez and coworkers [18] validated the breakthrough for 90 VOCs of interest such as chloroacetonitrile and pentachloroethane using Tenax/Carboxen 1000 at a flow rate of 22 mL/min for 2 hours to sample 2.64 L of air. All analytes passed the EPA recommended criteria for breakthrough and did not exceed 5%.

In Singapore, regular atmospheric monitoring of various volatile organic pollutants has not been carried out. The National Environment Agency, which is the leading public organization responsible for monitoring air quality in Singapore, only reports the PSI which is calculated based on 5 major atmospheric contaminants [particulates $< 10\ \mu\text{m}$ (PM_{10}), SO_2 , CO, tropospheric O_3 and NO_x], concentration measurements of the mentioned pollutants at specified intervals and concentration readings for $\text{PM}_{2.5}$ [19, 20]. In addition to that, Singapore suffers serious air quality problems annually from the burning of biomass by neighboring countries to create new land for palm oil plantations [21, 22].

In this chapter, an analytical method was developed and validated for evaluating the amounts of atmospheric VOCs that are commonly found in the western industrialized region of Singapore, which is the home to one of the largest petroleum refineries in the world. 48 compounds were selected as target analytes after identification from air samples collected by active sorbent-based sampling and evaluated using TD-GCMS prior to method optimization.

2.2 Experimental

2.2.1 Chemicals and Standard Solutions

Neat chemicals were purchased from Sigma-Aldrich (St Louis, USA), Merck (Hohenbrunn, Germany), Alfa Aesar (Heysham, Lancaster, UK) and Fluka (Buchs, Switzerland) with purity not less than 97%, except for 1,2,3-trimethylbenzene (93.9%) from Fluka and Methacrolein (95%) from Sigma-Aldrich. These chemicals were employed as VOC reference standards and individual VOC solutions (20% v/v) were prepared by dissolving 1 mL of neat chemicals in methanol (Tedia, Fairfield, USA) using 5 mL volumetric flasks.

Stock solutions (20% v/v) were diluted to 50 g/L solutions using the same solvent. A 500 ng/ μ L standard mixture was subsequently prepared by transferring 500 μ L from each 50 g/L individual VOC solutions into a common 50 mL volumetric flask, topped with methanol and homogenized. The 500 ng/ μ L VOC mixture was confirmed by experiments and evaluated to be stable for at least 8 days when stored at 4 °C in darkness. Further dilution of the mixture was carried out to make calibration standard solution, with various concentrations ranging from 0.02 to 500 ng/ μ L. All calibration standards were freshly prepared before an instrumental analysis from the 500 ng/ μ L mixture.

2.2.2 *Sorbent Tubes*

For this study, sorbent tubes (3.5 in. (89 mm) $\times$ 0.25 in. (6.4 mm) o.d.) packed with 200 mg of Tenax and 100 mg of Carbopack X (Markes International Limited, Llantrisant, U.K.) were used for injection of standards and collection of air samples. Multi-sorbent tubes are more capable of adsorbing an extensive range of analytes with differing polarities and boiling points compared to single sorbent tubes. Tenax is a weak strength sorbent that is specific for aromatics, non-polar VOCs with boiling points beyond 100 °C and polar analytes with boiling points below 150 °C. Carbopack X has a medium-to-strong sorbent strength and is selective for more volatile compounds, with boiling points between 50 °C to 150 °C. Both materials are hydrophobic and can minimize the effects of relative humidity on breakthrough. Sorbents were filled in order of increasing sorbent strength, each material divided by quartz wool, retaining gauzes and a retaining spring at the end tube. New sorbent tubes were conditioned at 320 °C for 2 hours, followed by 335 °C for 30 minutes for the first time, prior to usage. Successive conditionings after usage were performed at 320 °C for 30 minutes. All conditionings were conducted under helium flow of 70 mL/min.

The transfer of calibration standards to sorbent beds was carried out by injecting 1 μL of the standard solution into a multi-sorbent tube attached to a calibration loading rig, using a Gas Chromatography (GC) manual syringe. The GC syringe containing the solution was introduced into the sorbent tube with a stream of nitrogen gas (99.999%) flowing in the direction of the injection at 100 mL/min. The manual syringe needle was placed inside the loading rig for a short period of 20 to 30 seconds to ensure target analytes were completely vaporized. The nitrogen gas assists the adsorption of the VOC onto the sorbents and purges the solvent (i.e. methanol) out of the tube.

2.2.3 Instrumentation

A UNITY series 2 (Markes International Limited, Llantrisant, U.K.) was used for the TD process and an Ultra autosampler (Markes International Limited, Llantrisant, U.K.) was employed for automated analysis of several sorbent tubes. Figure 2.1 depicts the TD-GCMS instrument that was utilized. There are two stages in the thermal desorption process: primary desorption and secondary desorption. During primary desorption, VOCs were released from the sorbent beds when the tube was heated to 280 °C for 10 minutes. Concurrently, a stream of high purity helium (99.999%) at 45 mL/min was introduced through the tube.

Figure 2.1: TD-GCMS instrument used in this thesis.

All compounds desorbed from the multi-sorbent tube were transferred onto a hydrophobic Tenax Peltier trap using splitless mode. The trap was cooled at -10 °C during preconcentration. During secondary desorption, the helium flow through the cold trap was directed to the GC column. The trap was heated to 300 °C for 7 minutes at the fastest temperature ramp rate to bring the desorbed VOCs into the GC column (Agilent J & W 122-1564 260 °C 60 m × 250 µm × 1.4 µm DB-VRX) for the separation of VOCs, using a split flow of 6 mL/min (i.e. a split ratio of 5:1).

The GC oven was programmed at 30 °C for 12 minutes, increased to 60 °C at a rate of 30 °C/min, followed by an increment to 124 °C at 40 °C/ min. The oven was held at 124 °C for another 2 minutes, before increasing to the final temperature of 200 °C at 9 °C/ min. The GC oven was kept at that temperature for 3 minutes. High purity helium (99.999%) was utilized as the carrier gas in the column and a constant flow of 1.5 mL/min at the column inlet was applied. The interface temperature between the GC and MS was maintained at 250 °C. The mass spectrometer acquired scan mode data for a mass range between 35 and 300 amu. The ion source (70 eV electron impact) and quadrupole temperature were set at 230 °C and 150 °C respectively. Qualitative identification of target VOCs was carried out by comparing the retention times (t_R), relative abundance of the qualifier ions and quantifier ion to those of VOC standards. Target compound quantification from air samples collected was performed using an external calibration procedure. Calibration curves were plotted as a function of concentration based on the signal intensities of quantifier ions.

2.2.4. Tuning of Mass Spectrometer

The mass spectrometer was tuned prior to instrumental analysis using perfluorotributylamine (PFTBA) at m/z = 69, 219 and 502, followed by

bromofluorobenzene (BFB) at $m/z = 50, 69, 131, 219, 414$ and 502 . PFTBA is used to examine the general condition of the mass spectrometer whereas BFB tuning and evaluation are requirements for VOC analysis, recommended by EPA TO-17. Air and water leak checks ($m/z 18, 32, 44$) were conducted as well.

2.3 Results and Discussion

2.3.1 Confirmation of Target Analytes

10 L air samples were collected in September 2010 and during the transboundary haze pollution between 19th to 22nd October 2010. The haze, which had blown over from forest fires in Sumatra, had brought Singapore's air pollution to its highest level in four years [23]. The PSI readings were the highest during the period from the 19th to 23rd October 2010, with values between 80 to 96 [24-27]. The 24-hour PSI measurements for the haze period in 2010 were summarized in Table 2.1. Total ion chromatograms of samples can be found in Appendix 1, Figures A1.1 to A1.10. Potential target analytes were identified from the total ion chromatograms of samples by matching to the NIST library of compounds. Mass spectrums of unknowns in samples were matched to mass spectrums of known VOCs available in the NIST database using a probability-based matching (PBM) algorithm.

While PBM is useful for predicting and estimating the analyte identities, confirmations with standards are necessary. In addition, PBM is unable to accurately determine isomers

Table 2.1: 24-hour PSI readings for 19th to 23rd October 2010 for different regions of Singapore [24-27].

Date	24-hour PSI Reading					
	North	South	East	West	Central	Overall Singapore
19/10/10	51	39	33	56	39	33-56
20/10/10	70	72	63	80	67	63-80
21/10/10	72	84	77	83	79	72-84
22/10/10	87	92	95	96	93	87-96
23/10/10	82	79	73	81	81	73-82

Table 2.2: TD-GCMS parameters and conditions prior to optimization.

Thermal desorption Parameters		GCMS Parameters	
Tube desorption temperature (°C)	275	GC oven temperature gradient	35 °C for 10 minutes, increased to 140°C at a rate of 8 °C/min, followed by an increase to 220 °C at a rate of 12 °C/min, hold for 3 min.
Tube desorption time (min)	10	Column flow (mL/min)	1.5
Tube desorption split flow (mL/min)	none	Carrier gas	Helium (99.999% purity)
Tube desorption flow (mL/min)	30	Auxiliary temperature (°C)	250
Trap desorption temperature (°C)	300	Source temperature (°C)	230
Trap desorption time (min)	5	Quadrupole temperature (°C)	150
Trap desorption split flow (mL/min)	13.5	MS scan mode mass range (amu)	35- 300

with similar mass fragmentation patterns (i.e. identical relative abundances of fragmentation ions). 50 VOC neat chemicals were purchased and individual 100 ng/μL VOC solutions were prepared using methanol as the diluting solvent. 1 μL of the solutions were injected into separate sorbent tubes and analyzed for retention times, base ions and representative ions for qualitative analysis. The pre-optimized TD-GCMS method conditions are summarized in Table 2.2. Confirmation of the target compounds was conducted by comparing the t_R and relative mass ion abundances of unknowns from air samples and that of 100 ng VOC standard solutions analyzed individually. 48 VOCs were identified from the qualitative analysis and were established as analytes for ambient air monitoring. Mass spectrums of VOC standards for qualitative identification can be found in Appendix 1, Figures A1.11 to A1.58.

2.3.2 Determination of Temperature Program for Analyte Separation by GC Column

The initial temperature gradient of the GC oven was modified for improvements to the analytical resolutions between the 3 main groups of peaks: (i) The separation of hexane and 2-butanone, (ii) heptane and trichloroethylene (iii) the separation behavior of ethyltoluene isomers, benzaldehyde, 1,3,5-trimethylbenzene, decane, octanal and

benzonitrile. The temperature at the t_R was calculated from the modified temperature program while the analytical resolution, R_s , was calculated using equation 2.1:

$$R_s = \frac{1.1177(t_{R2}-t_{R1})}{w_{h1}+w_{h2}} \dots\dots\dots (2.1)$$

where t_{R1} and t_{R2} are retention times of peak 1 and peak 2, w_{h1} and w_{h2} are the peak widths at half height of peak 1 and 2. 50 ng VOC standards mix was loaded into separate Tenax/carbopack X sorbent tubes for evaluation of changes in peak separation when changes were made to the temperature gradient of the GC oven.

Analytical resolutions of VOCs in groups (i) and (ii) were modified first. Improvements in peak separation for all 4 compounds, represented as peaks A to D in Figure 2.2, were observed when changes were made to the temperature program. The initial temperature was reduced from 35 °C to 30 °C and held for 12 minutes instead of 10 minutes. Subsequent temperature rates after the initial oven temperature between 30 °C to 124 °C were modified to be steeper than the original gradient: 30 °C /min to 60 °C, followed by 40 °C /min to 124 °C held for 2 minutes and finally 9 °C/min to 200 °C held for 2 minutes. The analytical resolution of hexane (peak A) and 2-butanone (peak B) increased from 1.15 to 1.32, as the oven temperature at the t_R changes from 61 °C to 110 °C. Likewise, the analytical resolution of heptane (peak C) and trichloroethylene (peak D) increases from 1.24 to 1.86, when the oven temperature at the t_R was raised from about 100 °C to 127 °C.

Figure 2.2 shows the separation of VOCs in group (i) and (ii) that was obtained using the initial [Figure 2.2(a)] and modified [Figure 2.2(b)] temperature gradient. Table 2.3 summarized the oven temperatures at the t_{RS} for the 4 VOCs and their analytical resolutions before and after changes was made.

Figure 2.2: Comparison of the separation of (i) hexane (peak A) and 2-butanone (peak B) and (ii) heptane (peak C) and trichloroethylene (peak D) obtained using (a) the initial and (b) the modified temperature programs.

Table 2.3: VOCs in peak clusters, the oven temperatures at their t_R s and analytical resolutions in the modified temperature program for Peaks A to D.

Peak	Initial temperature gradient			Modified temperature gradient		
	Compound	Oven Temperature at t_R (°C)	Resolution	Compound	Oven Temperature at t_R (°C)	Resolution
A	hexane	60.10	1.15	hexane	108.40	1.32
B	2-butanone	60.98		2-butanone	110.40	
C	heptane	99.07	1.24	heptane	126.61	1.86
D	trichloroethylene	99.77		trichloroethylene	127.33	

Figure 2.3(a) shows the separation for VOCs in group (iii) namely: 3-ethyltoluene (peak E), 4-ethyltoluene (peak F) benzaldehyde (peak G), 1,3,5-trimethylbenzene (peak H), decane (peak I), 2-ethyltoluene (peak J), octanal (peak K) and benzonitrile (peak L) from the temperature program modified for hexane, 2-butanone, heptane and trichloroethylene.

Figure 2.3 (b) and (c) reveals the changes in separation for peaks E to L when the temperature gradient is varied. Table 2.4 summarizes the temperature at the t_R for each compound and the analytical resolution of the peaks of interest in Figure 2.3.

(a)

30 °C held for 12 min, 30 °C/min to 60 °C, 40 °C/min to 124 °C held for 2 min, 9 °C/min to 200 °C held for 2 min.

(b)

30 °C held for 12 min, 30 °C/min to 60 °C, 40 °C/min to 124 °C held for 1 min, 6 °C/min to 200 °C.

(c)

30 °C held for 12 min, 30 °C/min to 60 °C, 40 °C/min to 124 °C, 6 °C/min to 200 °C.

Figure 2.3: Separation of 3-ethyltoluene (peak E), 4-ethyltoluene (peak F), benzaldehyde (peak G), 1,3,5-trimethylbenzene (peak H), decane (peak I), 2-ethyltoluene (peak J), octanal (peak K) and benzonitrile (peak L) obtained using 3 temperature programs.

Table 2.4: VOCs in peak clusters, their temperatures at the t_R and analytical resolutions in the modified temperature program for Peaks E to L.

Peak	Compound	Temperature program in Figure 2.3(a)		Temperature program in Figure 2.3(b)		Temperature program in Figure 2.3(c)	
		Temperature at t_R (°C)	Resolution	Temperature at t_R (°C)	Resolution	Temperature at t_R (°C)	Resolution
E	3-ethyltoluene	178.00	(E/F) 1.44 (F/G) 1.21	166.26	(E/F) 1.51 (F/G) 1.21	169.21	(E/F) 1.48 (F/G) 1.34
F	4-ethyltoluene	178.72		166.78		169.69	
G	benzaldehyde	179.26		167.22		170.13	
H	1,3,5-trimethylbenzene	180.25	1.25	167.94	1.3	170.79	0.914
I	decane	180.70		168.44		171.20	
J	2-ethyltoluene	182.05		169.31		172.07	
K	octanal	182.77	(J/K) 1.49 (K/L) 1.06	169.92	(J/K) 1.67 (K/L) 0.857	172.56	(J/K) 1.33 (K/L) 1.20
L	benzonitrile	183.22		170.29		172.95	

Figure 2.3(b) shows the same group of compounds being separated using a hold time of 1 min at 124 °C, followed by 6 °C/min to 200 °C. The analytical resolution between 1,3,5-trimethylbenzene and decane peaks increases from 1.25 to 1.3 as the temperature at the t_R decreases from 181 °C to 168 °C. The resolution between octanal and benzonitrile, on the other hand, decreases from 1.06 to 0.857 as the temperature at the t_R reduces from 183 °C to 170 °C. Figure 2.3(c) shows the separation of those compounds using no hold time at 124 °C, followed by 6 °C /min to 200 °C. The analytical resolution between 1,3,5-trimethylbenzene and decane peaks reduces from 1.3 to 0.914 as the temperature at the t_R increases from 168 °C to 171 °C. The analytical resolution between octanal and benzonitrile, however, increases from 0.857 to 1.20 as the temperature at the t_R increases from 170 °C to 173 °C.

Several temperature gradients between 124 °C and 200 °C were also evaluated. Gentler temperature rates such as 4 °C/min and 5 °C/min show generally poorer resolution for octanal and benzonitrile. Likewise, steeper gradients such as 10 °C /min, 11 °C /min, 12 °C /min show no further improvements in the separation of 1,3,5-trimethylbenzene and decane, as well as that of benzonitrile and octanal. Therefore, the final temperature gradient was taken as 30 °C for 12 min, 30 °C/min to 60 °C, 40 °C/min to 124 °C held for 2 min, 9 °C /min to 200 °C maintained at 3 min.

Table 2.5: Different combinations of desorption time and temperature that were evaluated for trap optimization.

Desorption Time (min)	Trap Desorption Temperature (°C)					
2	250	260	270	280	290	300
5	250	260	270	280	290	300
7	250	260	270	280	290	300
10	250	260	270	280	290	300

Although not completely resolved from each other (ideal resolution should be 1.5 and above), each component has at least an analytical resolution of 1. The final temperature was maintained one minute longer because holding the final temperature of 2 minutes is insufficient for the final compound of interest to elute from the column. The extension of 1 minute allows decanal to register a signal on the GC chromatogram.

2.3.3. TD Method Optimization

Trap desorption parameters were optimized first to ensure complete desorption of VOCs from the trap. Incomplete trap desorption could result in inaccuracies when quantifying compounds of interest. Another reason is that the compounds remained in the trap could become potential interferences during the analysis of the next sorbent tube. Different combinations of trap desorption temperatures and times were evaluated while keeping all other thermal desorption parameters constant at the initial conditions. These combinations of different conditions are summarized in Table 2.5.

The trap desorption temperature was varied between 250 °C and 300 °C; while the trap desorption time was varied between 2 minutes to 10 minutes. Desorption from the trap was inspected by running a trap blank after running a tube loaded with 50 ng of 48 VOC calibration mix. The trap blank was obtained by performing a “trap heat method” in the UNITY thermal desorption autosampler with the exact same trap conditions used for evaluating the loaded tube prior to the trap blank. The selection for the optimized combination is based on two conditions: (i) Selected parameters must be able to desorb

high boiling compounds that could be present in air samples to avoid carryover or memory effects at the trap. (ii) Optimized parameters must be sufficiently long for complete desorption of target compounds but at the same time, be efficient and feasible for analysis.

As expected, longer desorption duration and higher temperature resulted in cleaner blanks being achieved. The blank chromatograms of all combinations tested (Figures 2.4- 2.7) show complete desorption of target analytes at the trap. However, high boiling point compounds are still detected in all chromatograms with desorption times of 5 minutes and below. They are minimized at 300 °C when desorbed at 7 minutes and removed completely between 280 °C to 290 °C when desorbed at 10 minutes. While the best blank was achieved when the trap was set at 300 °C and desorbed at 10 minutes, 10 minutes is too long for trap desorption. Therefore, 300 °C and 7 minutes were chosen as the optimized trap desorption temperature. Baseline offsets were also observed from trap blank chromatograms. These offsets are attributed to the switching of mechanical valves of the thermal desorption autosampler during the desorption stages.

Figure 2.4: Trap blanks obtained for varying desorption temperatures at 2 min.

Figure 2.5: Trap blanks obtained for varying desorption temperatures at 5 min.

Figure 2.6: Trap blanks obtained for varying desorption temperatures at 7 min.

Figure 2.7: Trap blanks obtained for varying desorption temperatures at 10 min.

Table 2.6: Split ratios calculated for the corresponding split flows at column flow of 1.5 mL/min.

Split flow (mL/min)	Split ratio
3	3:1
6	5:1
9	7:1
13.5	10:1

The trap split flow was optimized next to enhance response levels for each target analyte, with minimal artifact interferences present in blank chromatograms. Trap split flow was varied at splitless, 3 mL/min, 6 mL/min, 9 mL/min and 13.5 mL/min. Split ratios of the split flows chosen for optimization were calculated using equation 2.2 shown below:

$$\% \text{ Sample} = \frac{100D_f \cdot F}{(O_{sf} + F)(D_f + I_{sf})} \quad (2.2)$$

Where F is the column flow, D_f is the desorption flow, O_{sf} is the outlet split flow and I_{sf} is the inlet split flow. The split ratios corresponding to the split flows are summarized in Table 2.6. Running the trap in splitless mode gives the highest total ion current (TIC) signals for all compounds of interest. The target analytes are transferred completely from the thermal desorption autosampler to the GCMS at the column flow rate. The flow during splitless mode (i.e. column flow 1.5 mL/min) is too low for efficient transfer of compounds to the GCMS and could shorten the lifespan of the trap resin.

A split flow of 3 mL/min was also not chosen. Although it gives the best target VOC TIC responses after splitless mode, there will be simultaneous enhancements in the sorbent artifact TIC signals. Changing the split flow from the original 13.5 mL/min to 3 mL/min would increase the TIC signal intensities in the 50 ng VOCs and sorbent artifact by 3.3 times. Using a split flow of 6 mL/min instead could enhance the magnitude of the VOC signal response by 2 times. Concurrently, the TIC signals of artifacts found in the blanks could be reduced by 40% from the responses corresponding to a split flow of 3 mL/min.

Figure 2.8: Overlaid total ion chromatograms of second consecutive analysis of sorbent tubes at various tube desorption temperatures between 250 °C – 300 °C. 2- methylheptane peak was observed at 18.37 min in the 250 °C chromatogram during second desorption of the same tube.

Higher sorbent artifact TIC signals present in the blank chromatograms would result in poor accuracies for determining target analytes at much lower concentrations detected. 6 mL/min was chosen as a compromise split flow between signal enhancement and minimization of artifacts.

Investigations on various tube desorption parameters were carried out subsequently. The selection of tube desorption temperature is conducted by determining the highest temperature capable of desorbing VOCs with varying boiling points and simultaneously generating minimal artifact interferences from the sorbent materials. Tube desorption temperatures were varied from 250 °C to 300 °C, in steps of 10 °C. All tube desorptions were carried out for 10 minutes. Blank sorbent tubes were evaluated first, before loading the tube with 50 ng of the standard mixture. Each tube loaded with standards was also analyzed twice to test for carryover of target analytes.

The total ion chromatograms of the second desorption (refer to Figure 2.8) show that 2-methylheptane was not completely desorbed at 250 °C. The peak can be seen at a t_R of about 18.37 min. Complete desorption of 2-methylheptane was observed at all other temperatures tested. No significant variation in the TIC signals of the other target VOCs

Figure 2.9: Plot of quantifier ion abundance against temperature (°C) for artifacts found in blank Tenax/Carbopack X tubes.

was observed when different tube desorption temperatures were evaluated. However, the intensity of artifact peaks in the blank sorbent tubes increases proportionally with tube desorption temperatures. Figure 2.9 shows the temperature trend for the quantifier ion responses of sorbent artifacts.

The amount of benzene, toluene, xylene isomers, phenol, benzaldehyde and acetophenone found in blanks are especially important because these compounds are target analytes. Previous studies have mentioned that the sources of primary artifacts in Tenax are from chemical reactions with O₃ [15, 28-33]. While artifact interferences are reduced by thermal conditioning of tubes before usage, the tube desorption parameters during analysis can also impact on the generation of artifacts in blanks. Generally, an increment of 10 °C to the desorption temperature leads to no significant changes to the amount of toluene, with the exception from 280 °C to 290 °C. During that temperature transition, the quantifier ion abundance of toluene increases by about 1.5 times. As for benzene, the quantifier signal response increases by about 1.3 to 2.2 times with every 10 °C increment from 250 °C to 300 °C. *m,p*-xylene, *o*-xylene and phenol artifacts exhibits the most drastic

positive changes in signal intensities at two temperature transitions: (i) from 250 °C to 260 °C and (ii) from 280 °C to 290 °C. Benzaldehyde has an average increment rate of 1.4 times for every 10 °C, while acetophenone has an enhancement factor of 1.6 times for each positive increase in 10 °C. Therefore, 280 °C was selected as the optimum tube desorption temperature as a compromise between benzene artifact generation at higher temperatures and effective desorption of VOCs. The relatively high temperature could ensure complete desorption of the sorbent tube at high concentrations, with acceptable amounts of artifacts in blanks. All artifacts found in the 280 °C blank chromatogram were quantified using calibration curves constructed by direct injection of standards into the GCMS. These curves were constructed at concentrations between 0.02 ng and 10 ng. The average amounts of all artifacts are below 1 ng, within the acceptable artifact limits and have %RSD values lesser than 20% for n=4 sorbent tubes.

The tube desorption time for efficient transfer of VOCs and minimal artifact interferences in the blank tubes was investigated after the selection of the tube desorption temperature. Tube desorption time was evaluated at 4 different durations: 5 min, 7 min, 10 min and 12 min. All tube desorptions were performed at 280 °C. Blank sorbent tubes were evaluated first, before loading the tube with 50 ng of the standard mixture. Each tube loaded with standards was desorbed twice to test for carryover of target analytes. The chromatograms

Figure 2.10: Overlaid total ion chromatograms of second consecutive analysis of sorbent tubes at various tube desorption times between 5 minutes to 12 minutes. 2-methylheptane peak was observed at 18.37 min in the 5 minutes chromatogram during second desorption of the same tube.

obtained from the second analysis of the sorbent tube (refer to Figure 2.10) show that 2-methylheptane was not completely desorbed at 5 minutes. The TIC peak can be seen at t_R about 18.37 min. Complete desorption of 2-methylheptane was noted at all other tube desorption times. No changes in the TIC response of target analytes were observed when the tube desorption time was increased. However, the signal response of artifacts present in the sorbent tubes were noted to increase proportionally with tube desorption time.

Figure 2.11 shows how time affects the amounts of artifacts present in blank sorbent tubes. The only positive change noted for the toluene artifact is during the increase in desorption duration from 10 minutes to 12 minutes, where there is a corresponding increment in peak area (by about 1.9 times). As for benzene, the quantifier ion signal rises by an average factor of 1.5 times with every 2 minute addition to the desorption duration. Phenol demonstrated constant factor increments in quantifier ion responses, between 1.08 to 1.11 times with every 2 minute extension. The signal intensities of xylene isomers and acetophenone were noted to be relatively constant during the changes in tube desorption times, whereas the benzaldehyde quantifier ion signal was found to increase by an average rate of 1.4 times per 2 minute increment in desorption time. The amount of

Figure 2.11: Plot of quantifier ion abundance against time (min) for artifacts found in blank sorbent tubes.

benzene and phenol found in the blank exceeded the acceptable limit of 1 ng at the 12 minute tube desorption time. Therefore, 10 minutes was chosen as the optimum time required for tube desorption.

To ensure the maximum transfer of analytes from the first to the second stage, the primary desorption flow rate was tested between 30 mL/min to 50 mL/min, in steps of 5 mL/min. Figure 2.12 shows the TIC peak area for each compound of interest found in the chromatograms obtained at different primary desorption flow rates. The TIC peak areas for all compounds of interest increase and reach the maximum when the flow rate increases to 45 mL/min. At 50 mL/min, the TIC signals drop drastically in comparison to the ones obtained at 30 mL/min. Decreased signals are probably due to analyte breakthrough of the cold trap, leading to a large loss of compounds. No optimization was conducted for tube split flow. Splitless mode was implemented at this step to maximize the transfer of organic compounds to the cold trap. No split flow was applied during tube desorption because no improvements were expected by increasing or varying the split flow.

Figure 2.12: Plot of total ion peak area abundance against VOC analytes at different tube desorption flows (mL/min).

Figure 2.13: Total ion current chromatogram for 100 ng standard mixture. Corresponding VOC reference numbers are listed in Table 2.7.

Figure 2.13 shows the total ion current chromatogram for all 48 target VOCs analyzed using the optimized TD-GCMS procedure, while Table 2.7 shows the t_R of the VOCs, their quantifier ion, the identity and percentage abundance of qualifier ions.

Table 2.7: Table of target VOCs and their retention times (t_R), quantifier ions (Q1 and Q2) and qualifier ions. The numerical values inside the brackets of the qualifier ions are the percentage abundances relative to the base ion.

VOC Reference no.	Target Analytes	Quantifier Ion	Qualifier ions		t_R (min)
			Q1	Q2	
1	isopropyl alcohol	45	43 (17)	59 (5)	8.21
2	ethyl ether	59	45 (65)	73 (12)	8.80
3	isoprene	67	68 (69)	53 (54)	9.11
4	dichloromethane	84	49 (90)	86 (65)	10.27
5	2-methylpentane	71	43 (100)	42 (53)	13.01
6	methacrolein	70	41 (84)	39 (73)	13.25
7	3-methylpentane	57	56 (87)	41 (52)	13.63
8	hexane	57	41 (60)	43 (51)	14.21
9	2-butanone	72	43 (100)	57 (8)	14.26
10	trichloromethane	83	85 (67)	47 (17)	14.70
11	ethyl acetate	43	61 (19)	70 (15)	14.79
12	methylcyclopentane	56	69 (48)	41 (42)	15.05
13	cyclohexane	84	56 (95)	41 (43)	15.98
14	benzene	78	77 (22)	51 (12)	16.16
15	heptane	71	43 (100)	57 (64)	16.89
16	trichloroethylene	130	132 (97)	134 (31)	16.97
17	methyl methacrylate	69	41 (85)	39 (46)	17.27
18	methyl cyclohexane	83	55 (61)	98 (46)	17.58
19	methyl isobutyl ketone	43	58 (48)	85 (25)	17.95
20	pyridine	79	52 (47)	51 (21)	18.10
21	2-methylheptane	57	43 (78)	70 (26)	18.37
22	toluene	91	92 (64)	65 (10)	18.70
23	1-octene	55	41 (77)	70 (90)	18.88
24	octane	43	85 (71)	57 (49)	19.04
25	hexanal	56	57 (71)	72 (33)	19.14
26	tetrachloroethylene	166	164 (77)	129 (65)	19.58
27	furfural	96	95 (91)	39 (33)	19.95
28	ethylbenzene	91	106 (38)	77 (8)	20.63
29, 30	<i>m,p</i> -xylene	91	106 (56)	77 (12)	20.86

Table 2.7: Table of target VOCs and their retention times (t_R), quantifier ions (Q1 and Q2) and qualifier ions. The numerical values inside the brackets of the qualifier ions are the percentage abundances relative to the base ion (continued).

VOC Reference no.	Target Analytes	Quantifier Ion	Qualifier ions		t_R (min)
			Q1	Q2	
31	nonane	57	43 (91)	85 (48)	21.00
32	heptanal	70	55 (66)	57 (55)	21.16
33	styrene	104	103 (46)	78 (37)	21.29
34	<i>o</i> -xylene	91	106 (54)	105 (21)	21.39
35	phenol	94	66 (24)	65 (20)	22.38
36	3-ethyltoluene	105	120 (42)	91 (14)	22.60
37	4-ethyltoluene	105	120 (39)	91 (12)	22.68
38	benzaldehyde	105	106 (97)	77 (87)	22.74
39	1,3,5-trimethylbenzene	105	120 (62)	91 (11)	22.85
40	decane	57	43 (74)	71 (45)	22.90
41	2-ethyltoluene	105	120 (42)	91 (13)	23.05
42	octanal	41	43 (94)	57 (94)	23.13
43	benzonitrile	103	76 (32)	50 (10)	23.18
44	1,2,4-trimethylbenzene	105	120 (59)	91 (11)	23.41
45	1,2,3-trimethylbenzene	105	120 (51)	91 (10)	24.03
46	acetophenone	105	77 (66)	120 (27)	24.82
47	nonanal	57	41 (70)	70 (40)	25.03
48	decanal	57	41 (81)	70 (58)	27.03

2.3.4. Method Validation

Method validation was carried out by inspecting the following characteristics of the optimized TD-GCMS procedure for VOC analysis: selectivity, precision, linearity, breakthrough, sensitivity, tube desorption efficiency and accuracy. Table 2.8 summarizes the method validation data acquired for these analytical characteristics.

Selectivity is used to assess the modified temperature gradient for separating target VOCs at higher concentrations. The analytical resolutions obtained between all compounds of interest were calculated from a total ion chromatogram that was generated from a sorbent tube injected with 100 ng of standards. Excellent chromatographic separation was observed for most target VOCs. 37 compounds have TIC signals with resolution values of 1.5 and above. 10 compounds had TIC signals with resolutions between 0.745 to 1.33, but could still be quantitatively determined by selecting a characteristic ion absent in the compound that is eluting together with itself, as the quantifier ion. Only 1 co-elution (same t_R and mass spectra) was noted from the isomers *p*-xylene and *m*-xylene, which

Table 2.8: Summary of method validation data for standards where %RSD stands for percentage relative standard deviation , R²stands for linear regression coefficients for concentrations between LOQ to 500 ng, LOD is Limit of Detection, LOQ is Limit of Quantification. %RSD rounded to nearest whole number.

VOC Reference no.	Target Analytes	%RSD (n=6)	R ²	Breakthrough (%)	LOD (ng)	LOQ (ng)	Tube desorption efficiency (%)	Accuracy (%)
1	isopropyl alcohol	2	0.9971	1.14	0.01	0.04	100	61
2	ethyl ether	3	0.9988	0	0.38	1.28	100	71
3	isoprene	4	0.9986	0	0.08	0.27	100	80
4	dichloromethane	2	0.9983	2.13	0.03	0.09	99.7	72
5	2-methylpentane	3	0.9986	0	0.16	0.55	100	82
6	methacrolein	3	0.9963	0	0.05	0.16	99.7	66
7	3-methylpentane	3	0.9981	0.34	0.02	0.07	99.9	82
8	hexane	3	0.9991	0.53	0.04	0.12	99.5	64
9	2-butanone	2	0.9981	0.67	0.01	0.04	99.6	66
10	trichloromethane	2	0.9993	0.65	0.01	0.05	99.8	63
11	ethyl acetate	2	0.9994	<d.l.	0.04	0.13	99.8	99
12	methylcyclopentane	3	0.9994	0.26	0.01	0.04	99.7	86
13	cyclohexane	2	0.9995	0	0.05	0.16	100	81
14	benzene	2	0.9986	0	1.03	1.68	98.9	84
15	heptane	5	0.998	0	0.17	0.58	100	84
16	trichloroethylene	2	0.9989	0	0.01	0.02	100	73
17	methyl methacrylate	2	0.9971	0	0.08	0.26	99.7	67
18	methyl cyclohexane	2	0.9984	0	0.04	0.14	100	81
19	methyl isobutyl ketone	1	0.999	<d.l.	0.07	0.22	99.8	62
20	pyridine	5	0.9971	0	0.41	1.38	99.9	74
21	2-methylheptane	2	0.9998	0	0.06	0.21	99.9	86
22	toluene	5	0.9965	1.15	0.09	0.16	99.7	91
23	1-octene	1	0.9996	<d.l.	0.05	0.17	100	70
24	octane	1	0.9982	0	0.06	0.19	99.9	89
25	hexanal	2	0.9976	0.4	0.05	0.15	99.7	82
26	tetrachloroethylene	2	0.9985	0	0.01	0.03	100	71
27	furfural	4	0.9963	0	0.32	1.07	99.5	70
28	ethylbenzene	4	0.9998	0.2	0.01	0.02	99.8	82
29	<i>m,p</i> -xylene	1	0.9947	<d.l.	0.12	0.21	99.8	78
31	nonane	1	0.9998	0.07	0.07	0.23	99.9	79
32	heptanal	3	0.9951	1.05	0.05	0.15	99.7	55
33	styrene	3	0.9985	0.75	0.01	0.02	99.8	75
34	<i>o</i> -xylene	2	0.9991	0.46	0.03	0.06	99.8	83
35	phenol	2	0.9925	1.36	1.31	2.24	92.1	88
36	3-ethyltoluene	1	0.9917	<d.l.	0.02	0.06	99.8	108
37	4-ethyltoluene	2	0.9972	0	0.02	0.06	99.9	111
38	benzaldehyde	4	0.9909	1.55	0.65	1.25	98.9	88
39	1,3,5-trimethylbenzene	7	0.9994	0.28	0.01	0.04	99.8	65
40	decane	1	0.9996	<d.l.	0.04	0.13	99.9	104
41	2-ethyltoluene	2	0.9941	<d.l.	0.03	0.1	99.8	87
42	octanal	2	0.9993	0	0.08	0.27	99.6	74
43	benzonitrile	2	0.9983	0	0.05	0.16	99.3	113
44	1,2,4-trimethylbenzene	1	0.9996	0.08	0.02	0.07	99.7	90
45	1,2,3-trimethylbenzene	1	0.9999	<d.l.	0.03	0.09	99.8	92
46	acetophenone	4	0.9973	0.96	0.54	0.97	98.8	113
47	nonanal	6	0.9967	0.46	0.05	0.18	99.5	86
48	decanal	5	0.9943	1.02	0.07	0.25	99	102

have to be quantified together. Precision was evaluated by analyzing six sorbent tubes (n=6) loaded with 100 ng of VOC standards and calculating the percentage relative standard deviation (%RSD) of the VOC quantifier ion signals found in the chromatograms obtained from these tubes. Excellent repeatability was achieved for all target compounds. The %RSD values for all VOCs (Table 2.8) were below 10% and

comply to the EPA TO-17 performance criteria of $\leq 25\%$ [15, 28].

Calibration curves of VOC standards were constructed by plotting the integrated area under VOC quantifier ion signals against varying analyte concentration [34]. The linear relationship between the two functions was examined using the coefficient of determination, R^2 . The linearity of the multi-point calibration curve of VOC standards over an extensive range of concentrations was tested. All target analytes exhibited good linearity between 0.02 ng to 500 ng, with R^2 values ≥ 0.99 , for signal to noise ratios ≥ 10 (i.e. the limit of quantification). Table 2.8 shows the R^2 values for each compound that is between the limit of quantification to 500 ng.

Breakthrough was investigated to determine the retention capacity limits of selected sorbent materials during air sampling and injection of standards. It is defined as the percentage of VOC mass detected in the back sorbent tube when two sorbent tubes of the same type are connected in series. While breakthrough information of certain compounds in single sorbents are available from commercial suppliers, it is important to determine the breakthrough under the present sampling conditions where multi-sorbents are used. Two types of breakthrough were evaluated in this study: (i) during the loading of VOC standards via a stream of nitrogen gas for trapping compounds onto the sorbent materials (Table 2.8), and (ii) during the collection of air samples using calibrated air pumps (Tables 2.9 and 2.10). The latter will be elaborated further under the next section. The former was carried out by injecting a 1 μL aliquot of the 500 ng/ μL standard mixture into the front end of two Tenax TA/Carbopack X tubes connected in series. A stream of nitrogen gas (99.999% purity) was concurrently flowing into the connected tubes at 100 mL/min for 5 minutes during the loading of standards. The experiment was carried out at 25 °C and 45% relative humidity. Both tubes were analyzed and the peak area of the target compounds were quantified using the calibration curve established at concentrations

between 0.02 ng to 500 ng. Breakthrough values for each VOC was calculated as a percentage of the mass of VOC analyte present in the back tube, over the total mass of VOC detected in both tubes [15]. All compounds of interest demonstrated excellent breakthrough values of $\leq 5\%$ during the injection of VOC standards (Table 2.8). The breakthrough data reveals that there were minimal leakages of analytes from the front sorbent tube during the preparation of sorbent tube standards for a nitrogen gas flow of 100 mL/min.

Instrument sensitivity is evaluated by its limit of detection (LOD) and limit of quantification (LOQ). LOD is the minimum amount of analyte present in a sample that can be detected but not quantified as an accurate value [34]. LOQ is the minimum amount of analyte found in a sample that can be quantitatively established with reliable precision and accuracy [34]. The LOD and LOQ calculations were carried out using two approaches. For compounds of interest that were absent from blanks, LOD is the amount of analyte that produces a signal-to-noise ratio of 3, while LOQ is the amount of analyte that generates a signal-to-noise ratio of 10 [15, 29, 34]. Signal-to-noise ratios are attained from comparisons of measured analyte quantifier ion signals from samples with known low concentrations with those of blank samples, and determining the minimum concentration at which the analyte can be accurately detected. For target compounds that were present in blanks, LOD was calculated as the sum of the average amount of compound present and three times the standard deviation of the response in blanks ($n=7$) while LOQ was determined as the sum of the average amount of VOC in the blanks and ten times the standard deviation of the response in blanks ($n=7$) [18, 34]. LOD and LOQ values for each VOC analytes are summarized in Table 2.8.

Tube desorption efficiency examines the recovery of analytes from tube desorption and investigates whether there are any remaining VOCs in the sorbent tube after the first

analysis. In other words, it is used to evaluate whether the tube desorption parameters (i.e. temperature, time and flow) are efficient for maximal transfer of analytes to the GCMS. The sorbent tube, spiked with 200 ng of analyte mixture via a calibration loading rig was analyzed twice by TD-GCMS. Tube desorption efficiency is reported as the percentage of VOC quantifier ion peak area during the first TD-GCMS analysis over the sum of quantifier ion peak areas obtained for the analyte in both TD-GCMS analysis. High recoveries of more than 98% were obtained for all analytes, except phenol, which has a tube desorption efficiency of 92.1% (Table 2.8). Lower recovery of phenol may be due to greater binding interactions to the sorbents surfaces [15].

Method accuracy was calculated as the percentage recovery of the integrated area under the analyte quantifier ion signal obtained using TD-GCMS, compared to the analyte quantifier ion response area obtained by direct injection under the same split conditions into the GCMS [18]. Triplicate analysis of 500 ng of VOCs was conducted for both methods to determine the average response. Recoveries between 70% to 113% were achieved for most compounds of interest (refer to Table 2.8). 7 compounds have recoveries between 61% to 67% and they are: isopropyl alcohol, methacrolein, 2-butanone, trichloromethane, methyl methacrylate, methyl isobutyl ketone and 1,3,5-trimethylbenzene. Heptanal has the lowest recovery (i.e. 55%).

2.3.5. Performance Evaluation of Sorbent Tubes in Samples

The performance of sorbent tubes under real sampling conditions was investigated by a series of air sampling experiments, at different sampling flow rates (i.e. 30 mL/min, 50 mL/min and 70 mL/min) and sampling volumes (i.e 1 L, 5 L and 10 L). Reproducibility and breakthrough of target VOCs detected in air samples were calculated for each combination of sampling volume and flow rate utilized. This is to establish the optimal

sampling volume and flow rate for real sample collection. Two tubes were connected in series with a portable pump attached to the sorbent tube at the back end. All sampling pumps were calibrated with a flow meter prior to usage. The summary of percentage breakthrough measurements obtained for all sampling volumes and flow rates are tabulated in Table 2.9. The value of zero indicates that no analyte was detected in the back tube, while < q.l. and < d.l. represents the amounts of analyte in the back tube are below the limit of quantification and detection. The breakthrough of pyridine in Table 2.9 is listed as n.d. (not detected) because pyridine was undetectable during the sampling period. The percentage breakthrough values of the target VOCs found in samples were calculated the same way as the percentage breakthrough values for standards in section 2.3.4 [15]. A duplicate setup was made to investigate the reproducibility of the sampling procedure using portable sampling pumps. %RSD was used to express the reproducibility of the sampling. The percentage breakthrough values were found to be < 5% over all flow rates and volumes for most target analytes except isopropyl alcohol, ethyl ether, dichloromethane, methacrolein, toluene, decane, 2-ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, nonanal and decanal.

A uniform increment in breakthrough was expected when the sampling volume and flow rate increased. However, this was not always the case. For the certain compounds such as *o*-xylene and 1,2,4-trimethylbenzene, irregular trends were observed. There are a few possible reasons for the observed anomalous breakthrough data. Natural variations in temperature and relative humidity could potentially influence the breakthrough values. It is widely known that breakthrough values are dependent on temperature and relative humidity of the sampling environment [28]. Because the time period for the collection of air samples are different due to different sampling flow rates, significant changes in the combination of both factors (i.e. temperature and relative humidity) during the different

Table 2.9: Table of percentage breakthrough values for all sampling volumes and flow rates. <d.l. stands for the amount of VOC detected in the back tube is below detection limit, <q.l. represents the amount of VOC in the back tube is below quantification limit, 0 stands for no VOC detected in the back tube and n.d. represents not detected in sampling. RH stands for relative humidity.

Name of Target analytes	1 L sample volume			5 L sample volume				10 L sample volume			
	55% RH 31 °C 30 mL/min	55% RH 31 °C 50 mL/min	56% RH 30 °C 70 mL/min	42% RH 31 °C 30 mL/min	43% RH 31 °C 50 mL/min	42% RH 31 °C 70 mL/min	42% RH 31 °C 30 mL/min	44% RH 31 °C 50 mL/min	44% RH 31 °C 70 mL/min		
isopropyl alcohol	0	0	0	2.52	4.17	6.03	8.83	10.41	16.10		
ethyl ether	0	0	0	0	0	26.69	0	0	25.42		
isoprene	0	0	0	0	0	0	0	0	0.44		
dichloromethane	9.39	17.90	23.06	41.24	59.71	19.12	38.77	38.26	63.14		
2-methylpentane	0	0	0	0	0	0	0	0	0.30		
Methacrolein	0	<q.l.	0	0	9.09	0	0	0	2.86		
3-methylpentane	0	0	0	0	0	0	0	0	0		
hexane	0	1.18	1.96	0.26	0.78	0.79	0.57	0.80	0.66		
2-butanone	0	0	0	0	0	0	0	0	0		
trichloromethane	0	0	0	0	0	0	0	0	0		
ethyl acetate	0	0	0	0	0	0	0	0	0.49		
methylcyclopentane	0	0	0	0	0	0	0	0	0.27		
cyclohexane	0	0	0	0	0.00	0.44	0	0	0.48		
benzene	<q.l.	<q.l.	<q.l.	<d.l.	<q.l.	<d.l.	<d.l.	1.36	0.88		
heptane	0	0	0	0	0	0	0	0	0.77		
trichloroethylene	0	0	0	0	0	0	0	0	4.47		
methyl methacrylate	0	0	0	0	0	0	0	0	0		
methyl cyclohexane	0	0	0	0	0	0	0	0	0		
methyl isobutyl ketone	0	0	0	0	0	0	0	0	0		
pyridine	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.	n.d.	n.d.		
2-methylheptane	0	0	0	0	0	0	0	0	0		
toluene	3.41	2.43	6.98	0.18	0.89	0.62	0.44	0.93	1.50		
1-octene	0	0	0	0	0	0	0	0	0		

Table 2.9: Table of percentage breakthrough values for all sampling volumes and flow rates. <d.l. stands for the amount of VOC detected in the back tube is below detection limit, <q.l. represents the amount of VOC in the back tube is below quantification limit, 0 stands for no VOC detected in the back tube and n.d. represents not detected in sampling. RH stands for relative humidity (continued).

Name of Target analytes	1 L sample volume					5 L sample volume				10 L sample volume			
	55% RH 31 °C	55% RH 31 °C	56% RH 30 °C	42% RH 31 °C	43% RH 31 °C	42% RH 31 °C	43% RH 31 °C	42% RH 31 °C	44% RH 31 °C	42% RH 31 °C	44% RH 31 °C	44% RH 31 °C	44% RH 31 °C
	30 mL/min	50 mL/min	70 mL/min	30 mL/min	50 mL/min	70 mL/min	30 mL/min	50 mL/min	70 mL/min	30 mL/min	50 mL/min	70 mL/min	70 mL/min
octane	0	0	0	0	0	0	0	0	0	0	0	0	0
hexanal	0	0	0	0	0	0	0	0	0	0	0	0	0
tetrachloroethylene	0	0	0	0	0	0	0	0	0	0	0	0	0
furfural	0	0	0	0	0	0	0	0	n.d.	0	0	0	0
ethyl benzene	0.62	1.42	1.65	0.12	0.81	0.34	0.14	0.14	0.27	0.14	0.27	0.4	0.4
<i>p.m</i> -xylene	<d.l.	<d.l.	<d.l.	<d.l.	<q.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
nonane	0	0	0	0	0	0	0	0	0	0	0	0	0
heptanal	0	0	0	0	0	0	0	0	0	0	0	0	0
styrene	0	<q.l.	<q.l.	0	1.18	1.19	0	0	2.51	0	2.51	3.99	3.99
<i>o</i> -xylene	0	<q.l.	<q.l.	<q.l.	1.29	0.52	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	0.66	0.66
phenol	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
3-ethyltoluene	<d.l.	<q.l.	<q.l.	<q.l.	<d.l.	<q.l.	<d.l.	<d.l.	<lo.d.	<d.l.	<lo.d.	<d.l.	<d.l.
4-ethyltoluene	0	0	0	0	4.08	<d.l.	0	0	0	0	0	0	0
benzaldehyde	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
1,3,5-trimethylbenzene	0	0	0	0	0	0	0	0	0	0	0	0	0
decane	1.51	3.21	15.16	1.26	16.78	4.82	1.22	1.22	<d.l.	<d.l.	<d.l.	<q.l.	<q.l.
2-ethyltoluene	<d.l.	<d.l.	<d.l.	<d.l.	6.71	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
octanal	0	0	0	0	0	0	0	0	0	0	0	0	0
benzonitrile	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.
1,2,4-trimethylbenzene	<q.l.	2.73	5.27	1.21	5.27	1.51	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.	<q.l.
1,2,3-trimethylbenzene	0	<d.l.	<d.l.	<d.l.	6.23	<q.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
acetophenone	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.	<d.l.
nonanal	0	0	0	0	0	7.15	0	13.6	5.35	13.6	5.35	7.49	7.49
decanal	0	0	0	0	n.d.	0	0	7.34	3.79	7.34	3.79	6.87	6.87

time spans could affect the breakthrough values obtained. In Singapore, the average intra-day temperature over the last 77 years varies from 24 °C to 31 °C [35]. A ≤ 7 °C difference would not considerably alter breakthrough measurements as mentioned from previous studies [36, 37]. To minimize the effects of relative humidity that can fluctuate drastically at different times of the day, the hydrophobicity of sorbents becomes important for reducing moisture from competing for active adsorption sites on sorbent surfaces, with analytes molecules [28, 37, 38]. Tenax TA and Carbopack X have adequate hydrophobicity to withstand an extensive range of relative humidities from significantly impacting the breakthrough for different target compounds [37, 39-41].

Another possible explanation for the non-uniform variation in breakthrough readings with sampling volume and flow rate is the natural variation in the concentration of atmospheric VOCs at different times of the day. Errors from breakthrough calculation could happen when low amounts of analytes were detected in the front tube even though trace amounts were found in the back tube. 30 mL/min was chosen as the sampling flow rate because the majority of the compounds of interest demonstrated excellent breakthrough (i.e. $\leq 5\%$) at that flow rate. Another reason is that the mentioned breakthrough anomalies were observed in samples obtained at flow rates from 50 mL/min and 70 mL/min. Dichloromethane was the only target analyte that failed the acceptable breakthrough requirement of $\leq 5\%$ at all sampling volumes. The compound has a breakthrough value of 9.39% that exceeds the permissible criteria, even at the lowest sampling volume and flow rate tested.

Sampling volumes of 1 L and 5 L both at 30 mL/min have the highest number of target compounds that passed the breakthrough criteria. Table 2.10 summarizes the sorbent tube performance evaluation data for both sampling volumes. 5 L would be an advantageous choice as the optimal sampling volume because a high sampling volume reduces the

method detection and quantification limit for all target compounds. The sensitivity of the analytical procedure could be enhanced when the higher sampling volume was used for preconcentration of VOCs on sorbent materials. In addition, more preconcentration is necessary for some compounds to be detected. Some VOCs such as ethyl ether, methacrolein, methyl methacrylate, furfural were only detected in the 5 L samples and

Table 2.10: Summary of the sorbent tube performance in sampling at 30 mL/min at 1 L and 5 L.

Target Analytes	Sampling Volume of 5 L				Sampling Volume of 1 L			
	Breakthrough (%)	% RSD (n=2)	MDL ($\mu\text{g m}^{-3}$)	MQL ($\mu\text{g m}^{-3}$)	Breakthrough (%)	% RSD (n=2)	MDL ($\mu\text{g m}^{-3}$)	MQL ($\mu\text{g m}^{-3}$)
isopropyl alcohol	2.52	1	0.002	0.008	0	2	0.01	0.04
ethyl ether	0	5	0.08	0.26	n.d.	n.d.	n.d.	n.d.
isoprene	0	14	0.02	0.05	0	8	0.08	0.27
dichloromethane	41.24	6	0.006	0.02	9.39	10	0.03	0.09
2-methylpentane	0	3	0.03	0.11	0	5	0.16	0.55
methacrolein	0	7	0.01	0.03	n.d.	n.d.	n.d.	n.d.
3-methylpentane	0	5	0.004	0.01	0	4	0.02	0.07
hexane	0.26	1	0.008	0.02	0	1	0.04	0.12
2-butanone	0	15	0.002	0.008	0	8	0.01	0.04
trichloromethane	0	2	0.002	0.01	0	12	0.01	0.05
ethyl acetate	0	18	0.008	0.03	0	11	0.04	0.13
methylcyclopentane	0	2	0.002	0.008	0	4	0.01	0.04
cyclohexane	0	3	0.01	0.03	0	1	0.05	0.16
benzene	<d.l.	3	0.21	0.34	<d.l.	7	1.03	1.68
heptane	0	6	0.03	0.12	0	6	0.17	0.58
trichloroethylene	0	9	0.002	0.004	0	7	0.01	0.02
methyl methacrylate	0	1	0.02	0.05	n.d.	n.d.	n.d.	n.d.
methyl cyclohexane	0	0	0.008	0.03	0	2	0.04	0.14
methyl isobutyl ketone	0	3	0.01	0.04	0	0	0.07	0.22
pyridine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2-methylheptane	0	7	0.01	0.04	0	5	0.06	0.21
toluene	0.18	7	0.02	0.03	3.41	5	0.09	0.16
1-octene	0	5	0.01	0.03	0	9	0.05	0.17
octane	0	4	0.01	0.04	0	12	0.06	0.19
hexanal	0	3	0.01	0.03	0	2	0.05	0.15
tetrachloroethylene	0	3	0.002	0.006	0	2	0.01	0.03
furfural	0	7	0.06	0.21	n.d.	n.d.	n.d.	n.d.
ethylbenzene	0.12	3	0.002	0.004	0.62	4	0.01	0.02
<i>m,p</i> -xylene	<d.l.	6	0.02	0.04	<d.l.	4	0.12	0.21
nonane	0	9	0.01	0.05	0	0	0.07	0.23
heptanal	0	18	0.01	0.03	0	11	0.05	0.15
styrene	0	0	0.002	0.004	0	5	0.01	0.02
<i>o</i> -xylene	<q.l.	2	0.006	0.01	0	4	0.03	0.06
phenol	<d.l.	0	0.26	0.45	<d.l.	17	1.31	2.24
3-ethyltoluene	<q.l.	4	0.004	0.01	<d.l.	9	0.02	0.06
4-ethyltoluene	0	11	0.004	0.01	0	9	0.02	0.06
benzaldehyde	<d.l.	6	0.13	0.25	<d.l.	12	0.65	1.25
1,3,5-trimethylbenzene	0	8	0.002	0.008	0	7	0.01	0.04
decane	1.26	9	0.008	0.03	1.51	8	0.04	0.13
2-ethyltoluene	<d.l.	7	0.006	0.02	<d.l.	2	0.03	0.1
octanal	0	6	0.02	0.05	0	10	0.08	0.27
benzonitrile	<q.l.	8	0.01	0.03	<q.l.	16	0.05	0.16
1,2,4-trimethylbenzene	1.21	8	0.004	0.01	<q.l.	4	0.02	0.07
1,2,3-trimethylbenzene	<d.l.	5	0.006	0.02	0	7	0.03	0.09
acetophenone	<d.l.	5	0.11	0.19	<q.l.	11	0.54	0.97
nonanal	0	0	0.01	0.04	0	5	0.05	0.18
decanal	0	18	0.01	0.05	0	15	0.07	0.25

were absent when preconcentrated at 1 L. 1 L would be preferred however, if the target analyte have consistently higher concentrations in the sampling environment. Dichloromethane was the only analyte that displayed high breakthroughs at all sampling volumes and flow rates. The breakthrough of pyridine could not be determined because it was not detected during the sampling period in all sampling volumes used for preconcentration (i.e. 1 L, 5L and 10 L).

Sorbent trapping of atmospheric VOCs using calibrated portable pumps was shown to be highly reproducible for all compounds of interest at sampling volumes of 1 L and 5 L at 30 mL/min. All 47 target VOCs (including dichloromethane) present in samples met the EPA TO-17 guidelines for reproducibility and have %RSD values $\leq 20\%$ (Table 2.10) for $n=2$.

The method detection limits (MDL), method quantification limits (MQL), breakthrough and %RSD values of the VOCs at 30 mL/min are summarized in Table 2.10. The MDL of target analytes was calculated based on the sampling volume. The LOD in Table 2.8 was divided by the chosen sampling volume to obtain the MDL. With the exception of pyridine, all target analytes satisfy the EPA TO-17 requirement, with MDLs < 0.5 ppbv for both sampling volumes. Isopropyl alcohol, 2-butanone, trichloromethane, methylcyclopentane, trichloroethylene, tetrachloroethylene, ethylbenzene, styrene and 1,3,5-trimethylbenzene at a sampling volume of 5 L have the lowest MDL at $0.002 \mu\text{g m}^{-3}$ whereas phenol has the highest MDL at $0.262 \mu\text{g m}^{-3}$. The MQL of target analytes was determined by division of the LOQ found in Table 2.8 and the selected sampling volume. Trichloroethylene, ethylbenzene and styrene at a sampling volume of 5 L have the lowest MQL at $0.004 \mu\text{g m}^{-3}$ whereas phenol has the highest MQL at $0.448 \mu\text{g m}^{-3}$.

2.4 Conclusion

A TD-GCMS method has been developed for the detection and quantification of 46 atmospheric VOCs frequently present in the western semi-urbanized region of Singapore, located in close proximity to petrochemical and heavy industries. 48 VOCs were assessed and validated for several analytical method characteristics. Excellent repeatability with %RSD values $< 10\%$, good linearity with $R^2 \geq 0.99$ for a wide range of concentrations between 0.02 to 500 ng, percentage breakthrough values 5% or lower, tube desorption efficiencies near to 100% and good recoveries between 61% to 120% were noted for all analytes.

Different sampling volumes and flow rates were utilized for evaluating the performance of the multi-sorbent tubes. 30 mL/min was selected as the optimal flow rate while sampling volumes 1 L and 5 L showed the best results in analytical performance (i.e. reproducibility and sampling breakthrough). The majority of the VOCs of interest demonstrated acceptable breakthrough $\leq 5\%$, reproducibility $\leq 20\%$ deviation and method detection limits < 0.5 ppbv. Criteria established by the EPA for sorbent tube sampling (EPA TO-17) were complied with for most analytes of interest.

Dichloromethane failed the breakthrough guidelines during air sampling, but this is common for the Tenax and Carbopack X sorbents. Pyridine was not detected in the environment during sampling breakthrough experiments. The previous detection of pyridine was when the air quality was affected by the annual transboundary haze pollution caused by Indonesian forest fires and when the sampling volume prior to optimization was much higher (i.e. 10 L) initially. The selection of sampling volume, breakthrough, reproducibility, MDL and MQL values for pyridine remain unknown.

With a versatile method optimized, developed and validated for detecting VOCs, further studies were implemented for the monitoring the air quality in the industrialized region in western Singapore, understanding the concentration patterns of these compounds that are present in the atmosphere at various time periods, and predicting sources of these compounds. These additional environmental studies are described in Chapter 3.

2.5 References

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Trend Profiles, Source Determination and Health Risk Assessment of Atmospheric Volatile Organic Pollutants in the Largest Industrial Complex in Southeast Asia from a Semi Urban Sampling Site

3.1 Introduction

Air pollution has been a major concern for Singapore over the last two decades. Rapid industrialization in the city-state nation has been ongoing since its independence and there is a growing necessity to monitor the levels of gaseous emissions generated by industries, motor vehicles and other urban anthropogenic activities. In addition, Singapore suffers from severe transboundary haze pollution annually due to the smoke from forest fires in neighboring countries that were started to create areas for palm oil plantations [1]. The NEA, Singapore's primary government organization in charge of monitoring the air quality nationwide, regularly reports six major atmospheric contaminants: CO, NO_x, O₃, PM₁₀, PM_{2.5} and SO₂ [2]. An air quality indicator known as the PSI is calculated by the agency as well, based on all monitored pollutants, except PM_{2.5} [3]. There are a total of 14 monitoring stations located island-wide that are recording these measurements [4].

Atmospheric studies conducted in Singapore have heavily emphasized understanding the local environment during smoke events caused by burning forests in neighboring nations. Direct sampling techniques and model simulations have both been employed in the literature. Koe et al. used prediction models to simulate the possible sequences of emission events [5]. Atwood and coworkers utilized direct measuring devices such as

particulate samplers, sun photometers, filter gravimetry and nephelometers. They also used trajectory-ancillary modeling and data products to evaluate the locations and sources of fires during the haze period in 2009 [6]. Mukherjee and Viswanathan studied the proportions of CO from biomass burning and local traffic using dispersion modeling. The modeled values obtained were based on CO emission factors as a function of speed and were analyzed against real sample measurements taken [7]. He et al. evaluated the impact of biomass burning on the urban atmospheric composition of semi-VOCs such as plant-wax n-alkanes, polycyclic aromatic hydrocarbons (PAHs) and polar organics [8].

Other than biomass burning studies, air quality investigations were carried out for monitoring trace metals, ions, PAHs, aqueous-soluble organics, elemental and organic carbons present in outdoor PM_{2.5} [9-11]. Some of the constituents found in particles were determined in specified microenvironments. Kalaiarasan et al. assessed the amounts of PAHs within particulates in multi-storey public housings [12]. See and various co-workers have quantified the organics, ions and metals of PM_{2.5} from cooking techniques in a residential kitchen [13] as well as investigated PAHs in particulates emitted from diesel vehicles [14].

There are few publications which describe monitoring ambient organic contaminants in Singapore even though the class of compounds is considered as one of the major criteria pollutants by environmental agencies around the world [15-17]. Lim and colleagues collected samples of moss to evaluate persistent organic compounds such as polychlorinated biphenyls (PCBs) which are employed as biomarkers of air pollution [18]. He and colleagues have monitored gaseous emissions of semi-VOCs, as well as those found in water [19]. As far as we know, there is a lack of information about the more volatile organic species found in the atmosphere as previous reports were associated with monitoring particulates and heavier organic molecules.

The determination of VOCs has been conducted in several countries around the world and has been incorporated into the routinely regulated list of air pollutants. Environmental agencies such as the EPA and the European Environment Agency (EEA) emphasizes primarily on NMVOCs that contribute to the production of tropospheric O₃ [20, 21]. Countries such as South Korea [22], Japan [23] Taiwan [24] and North America [25] have undertaken VOCs monitoring studies in the ambient air.

The objective of this study is to monitor ambient VOCs present in a semi-urban sampling site that lies between one of the largest industrial estates in Southeast Asia and a forest used for occasional military exercises, situated in western Singapore. In this chapter, the concentration trend profiles, monthly and annual statistics for 46 target VOCs were determined. The analytical method that was described in Chapter 2 is used for this study. The source profiles of hydrocarbons were estimated by correlation coefficients and predicted by positive matrix factorization modeling. A health risk assessment was also performed for some VOCs for non-cancer and cancer effects.

3.2 Experimental

3.2.1 Sampling Location

The collection of air samples was performed on the roof of the School of Physical and Mathematical Sciences building (SPMS) within Nanyang Technological University, situated in the western region of Singapore. The vicinity in the south and east direction of the school building comprises of a portion of the Pan-Island Expressway (PIE) and residential estates. Both are located 100 m and 260 m away from the SPMS, respectively. In addition, the SPMS is 1.77 km from the nearest factories in Tuas, the largest industrial complex in Singapore and 5.75 km from one of the world's largest petroleum refineries in Jurong Island [26]. Various types of manufacturing industries such as petrochemical

refining, rubber vulcanizing and plastic molding process plants, food and beverages factories, pharmaceuticals and medical technology companies are found in Tuas [27-30]. A renewable diesel production plant, biggest in the world and capable of generating 800,000 tons per annum of diesel, using palm oil as feedstock, is also located in the industrial zone [31, 32].

Two of Singapore's four main incineration plants are also in Tuas and they are Tuas Incinerator [33] and Tuas South Incinerator [34]. Less than 1 km to the west of the SPMS lies a forest used for occasional military exercises. The forest borders the north and west of the university, in contrast to the industries and residential neighborhoods situated to its south and east. The geographical proximity of the sampling site, residential areas, the natural forest and industries present in Tuas and Jurong Island makes it ideal for investigating the VOC concentration patterns in such a complex environment. Regular monitoring at this semi urban sampling location would provide valuable information on the concentration levels and patterns of atmospheric volatile organics emitted from several sources. Figure 3.1 shows the map of the sampling site and landmarks mentioned above.

Figure 3.1: Map of Tuas Industrial Estate and Jurong Island. Green shaded area represents residential areas situated near the sampling site.

3.2.2 *Sample Collection*

Atmospheric VOC samples were collected using multi-sorbent tubes [3.5 in. (89 mm) × 0.25 in. (6.4 mm) o.d.] packed with 200 mg of Tenax and 100 mg of Carbopack X (Markes International Limited, Llantrisant, U.K). A total of 517 air samples, collected at a sampling volume of 5 L, were acquired between 1st February 2012 to 31st January 2013 using a MTS-32TM sequential tube sampler equipped with a SKC Pump set at a flow of 30 mL/min. 4 samples were collected per day at 10.52 AM, 16.22 PM, 21.52 PM and 3.22 AM for a time period of 2 hours and 45 minutes. The performance of the sampling procedure has been validated in Chapter 2 (Refer to Section 2.3.5).

3.2.3 *Chemical Reagents and Standards*

Due to failure of detection or method validation criteria mentioned in the Chapter 2, 2 VOCs namely: dichloromethane and pyridine were omitted from the monitoring experiments. 46 VOC solutions (20% v/v) were made in 5 mL volumetric flasks using methanol (Tedia, Fairfield, USA) as solvent from their neat chemicals, which were purchased from various commercial suppliers: Sigma-Aldrich (St Louis, USA), Merck (Hohenbrunn, Germany), Alfa Aesar (Heysham, Lancaster, UK), Fluka (Buchs, Switzerland) and Acros Organics (Japan) with at least 97% purity. Two other VOCs, namely: 1,2,3-trimethylbenzene and methacrolein, have 90% purity and were obtained from Sigma-Aldrich (St Louis, USA). Individual stock solutions were further diluted to 50 g/L solutions, followed by an extraction of 500 µL from each 50 g/L solutions into a 50 mL volumetric flask to form a 500 ng/µL mixture of 46 VOCs. Calibration standards were formed by performing additional dilution steps to the 500 ng/µL mixture.

3.2.4 *Analytical Instrument*

All sorbent tubes were evaluated using TD-GCMS. A UNITY series 2 (Markes International Limited, Llantrisant, U.K.) and an Ultra autosampler (Markes International Limited, Llantrisant, U.K.) were utilized for executing the TD process and for automating the analysis of multiple sorbent tubes respectively. During the tube desorption stage, VOCs were thermally desorbed from the sorbent tubes at 280 °C for 10 minutes and transported to the cold trap maintained at -10 °C, using a flow of high purity helium (99.999%) set at 45 mL/min. The stream of helium was inverted and the trap temperature was increased to 300 °C at the fastest rate possible for 7 minutes during the trap desorption stage. This was to transfer the VOCs from the cold trap to the Agilent 7890A GC attached to a 5975C inert MS (Agilent Technologies, USA). The analytes enter the GC column (Agilent J & W 122-1564 260 °C 60 m × 250 µm × 1.4 µm DB-VRX) for separation at a split flow of 6 mL/min. The GC oven temperature was programmed initially at 30 °C for 12 minutes, subsequently to 60 °C at 30 °C/min, followed by another increment to 124 °C at 40 °C/min. The oven was maintained at 124 °C for another 2 minutes, before elevating to 200 °C at 9 °C/min. The GC oven was then held constant at the final temperature for 3 minutes. Constant flow of 1.5 mL/min was used for the GC column. The auxiliary temperature between the GC and MS was maintained at 250 °C. MS data acquisition was carried out in scan mode between 35 to 300 amu. The ion source (70 eV electron impact) and quadrupole temperatures were kept at 230°C and 150°C respectively.

3.2.5 *Analytical Method*

The analytical method had been validated for the following characteristics described in Chapter 2 (refer to section 2.3.4): Selectivity, Precision, Linearity, Breakthrough,

Sensitivity, Tube Desorption Efficiency and Accuracy.

3.2.6 Statistical Methods

For statistical calculations (eg. Spearman correlation coefficients ρ and coefficients of determination R^2) and the plotting of daily concentration trends and monthly box-and-whiskers diagrams, Origin Pro 8.1 and Microsoft Excel 2007 were used. Sample mean of VOC X , also known as $\bar{X}$, was calculated using equation 3.1,

$$\bar{X} = \frac{\sum_{i=1}^n X_i}{n} \dots\dots\dots (3.1)$$

where n is the total number of samples and X_i are the concentration values i of the VOC X .

The Spearman correlation coefficient ρ , is the Pearson correlation coefficient between the ranked variables. For n total number of samples, paired concentration datasets (X_i, Y_i) are transformed into ranked variables (x_i, y_i) . The Spearman correlation analyzes the strength and direction of the relationship between the two variables using a monotonic function.

The calculation is performed using equation 3.2,

$$\rho = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2} \sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}} \dots\dots\dots (3.2)$$

where x_i and y_i are the ranks of the different concentrations of VOC X and Y , respectively, and $\bar{x}_i$ and $\bar{y}_i$ are the means of the ranked variables of VOC X and Y . The values of ρ ranged from -1 and +1. + ρ represents a positive correlation between VOC X and Y : When values of X rise there is a corresponding increase in values of Y . On the other hand, - ρ indicates a negative correlation between VOC X and Y : When values of X increase, values of Y are shown to decrease. A ρ value of zero implies there is no tendency for Y to either increase or decrease when X increases. Magnitude increments of the Spearman correlation represents that the X and Y variables become closer to being ideal monotone functions of

each other.

The coefficient of determination, R^2 , between paired concentration datasets (X_i, Y_i) is calculated by using equation 3.3,

$$R^2 = \left[\frac{\sum_{i=1}^n (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^n (X_i - \bar{X})^2} \sqrt{\sum_{i=1}^n (Y_i - \bar{Y})^2}} \right]^2 \dots\dots\dots (3.3)$$

where n is the total number of samples, X_i and Y_i are the different concentration values of the VOC X and Y , respectively, and $\bar{X}$ and $\bar{Y}$ are the sample means of the two VOCs. R^2 examines the goodness of fit of the linear regression for the paired data set. Its values extend between 0 to 1. These calculations present the proportion of variance for one variable that is expected from the other variable.

3.2.7 Modeling Method

EPA PMF 3.0 multivariate receptor modeling was utilized to determine: (i) the number of sources p that best described the observed VOC concentration at the sampling location and (ii) the VOC mass contribution to each source, for all 517 samples that were acquired over the span of one year. The modeling software is based on the Positive Matrix Factorization (PMF) method developed by Pentti Paatero [35]. PMF is mathematically expressed in component form as equation 3.4: An experimental data matrix with m samples and n species, the quantified amounts of each species can be described in terms of the contribution from p independent sources to all species found in a sample provided.

$$x_{ij} = \sum_{p=1}^p g_{ip} f_{pj} + e_{ij} \dots\dots\dots (3.4)$$

Where x_{ij} is the j th species concentration in $\mu\text{g m}^{-3}$ measured in the i th sample, g_{ip} is the mass contribution in $\mu\text{g m}^{-3}$ from p th factor to the i th sample, f_{pj} is the mass fraction of

Table 3.1: Equations used for calculating concentrations (x_{ij}) and uncertainties (u_{ij}) for different ranges of x_{ij} . $\bar{x}_j$ is the geometric mean of the samples greater than the MDL of the j th species and u_{ij} the uncertainty estimated in the j th species present in the i th sample. 0.15 is taken from the uncertainty of reproducibility [41].

Concentration (x_{ij}) equation	Uncertainty equation (u_{ij}) for x_{ij}	Valid concentration range
x_{ij}	$DL_j/3 + 0.15x_{ij}$	$x_{ij} \geq DL_j$
$DL_j/2$	$5/6 DL_j$	$x_{ij} \leq DL_j$
$\bar{x}_j$	$4\bar{x}_j$	$x_{ij} = 0$

j th species from p th source, and e_{ij} is the residual associated with the concentration of the j th species in the i th sample [36]. Penalty functions incorporate non-negative restrictions to the elements of the factor matrices defining the mass contribution of the identified sources and the characterization of each source [37]. The benefit of using PMF modeling is that each data point can be weighed individually [38]. Manual modifications are permitted to the concentration and uncertainty values for absent species or species below their method detection limits (MDL), represented as DL_j in the equations in Table 3.1, such that they do not significantly impact the final solution [39, 40]. The equations employed for concentration and uncertainty calculations are tabulated in Table 3.1.

VOC signal to noise ratio can be calculated with equation 3.5 in accordance with the concentration and uncertainty inputs into the PMF software:

$$\left(\frac{S}{N}\right)_j = \sqrt{\frac{\sum_{i=1}^n (x_{ij} - s_{ij})^2}{\sum_{i=1}^n s_{ij}^2}} \dots\dots\dots (3.5)$$

Equation 3.5 is used to verify whether the variability in the measurements is real and within the noise of the data. VOC species are classified as “bad”, “weak” and “strong” according to their signal-to-noise ratios and their percentage of concentrations beneath the MDL [42]. Compounds that are categorized as “bad” are removed from the PMF

modeling. Exclusion of analytes is made when: (i) signal-to-noise values are < 0.2 and/or (ii) $\geq 35\%$ of concentrations are below the MDL.

PMF minimizes the weighted sum of squares $Q(E)$ to solve equation 3.4 with a robust mode, mathematically defined as equation 3.6:

$$Q(E) = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{u_{ij}} \right)^2 = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{x_{ij} - \sum_{p=1}^p g_{ip} f_{ip}}{u_{ij}} \right)^2 \dots\dots\dots (3.6)$$

A total 25 target VOCs (i.e. straight-chain, cyclic and aromatic hydrocarbons) were modeled by PMF. All 46 VOCs were initially modeled together but due to poor R^2 values observed for alcohols, carbonyls and chlorinated species, they were removed and eventually only hydrocarbons, the major constituents of organic air pollutants were modeled. Different solutions between 3 to 11 factors were evaluated. Two approaches were used to investigate the optimal number of factors (i.e. sources): (i) Q value analysis and (ii) Scaled residuals analysis. All Q functions are quality of fit parameters. The PMF software generates a Q(Robust) and Q(True) value for p number of factors. Q(Robust) is calculated without samples that have scaled residuals > 4 . As for the Q(True) values, all samples are incorporated, including those outlier samples. Q theoretical which is not processed by the EPA PMF 3.0 model but can be approximated by the equation 3.7.

$$Q_{theoretical} \approx nm - p(n + m) \dots\dots\dots (3.7)$$

In equation 3.7, n represents the number of VOC species included in the model, m is the number of samples in the data set and p is the number of factors that fitted the model. The goodness of fit between the Q(Robust) to the Q(True) value indicates that the Q-values are very stable. The optimal solution should have a Q(Robust) within 1% of the Q (True) and $\pm 50\%$ of the Q theoretical. All possible solutions that attained convergence and a good quality of fit for all the mentioned criteria of the Q values were inspected further.

Residual analysis was used to investigate the possible solutions. Frequency of scaled residuals against the scaled residual values were plotted by the modeling software and analyzed. When the input data matrix and model are well-fitted, there should be minimal negative or positive discrepancies in the scaled residual distribution. All modeled VOCs should have scaled residuals situated from -3 to +3. The observed/predicted scatter plot has to be examined and the R^2 of the predicted concentration against the observed concentration should be > 0.6 .

7 factors was selected as the optimal solution for the 25 aliphatic, cyclic and aromatic hydrocarbon analytes based on the base model runs optimization as its factor profiles give the most reasonable explanation to the observed concentration. All criteria mentioned above were met. The convergence of Q(E), the Q(Robust) and Q(true) values deviating by less than one unit, indicates that a very stable solution was obtained. The Q(Robust) was within $\pm 50\%$ of the Q theoretical. The Q values obtained for each factor during factor optimization are summarized in Appendix 2 Table A2.1. Furthermore, the correlations between the predicted and observed concentrations were all > 0.6 and all standardized scale residuals were between ± 3 (Appendix 2, Table A2.2 and Figure A2.44). Bootstrap analysis was conducted for 100 runs with a minimum correlation R-value of 0.6 and a block size of 4. At least 97 bootstrap factors were mapped to the base factors indicating that the bootstrap result is stable (Appendix 2, Table A2.3).

Fpeak modeling in PMF controls factor rotation. To minimize rotational ambiguity, Fpeak values ranging between -1 to +1 were explored, in intervals of 0.1. The optimal solution should be between the Fpeak range in which the object function Q(E) remains relatively constant [43]. To examine the changes in Q functions, the plots of Q(Robust) and Q (True) were plotted against Fpeak to determine the Fpeak value prior to sudden increment in the Q function value (Appendix 2, Figure A2.45 and A2.46). It was found that steep

transitions of the Q values, particularly Q(True), occur when the Fpeak is > 0.4. No significant variation in Q functions when Fpeaks were between -0.2 to 0.2. A positive, non-zero Fpeak value generally generates more realistic results for an environmental data set [41]. Hence, a Fpeak value of 0.1 was selected for this study after the G-space plots were analyzed for unrealistic linear transformations. The slight change in source profiles using that Fpeak value demonstrates better agreement with the observed VOC concentrations. The procedures mentioned above were iterated for 8 factors to reaffirm that the main factor profiles do not have significant alterations.

3.2.8 Risk Assessment

To estimate the danger levels of individuals that are chronically exposed to non-carcinogenic and carcinogenic VOCs, risk assessments were carried out to investigate these effects in different VOCs. Non-cancer risk assessment was evaluated by calculating the hazard ratio (HR_i) of the VOC species using equation 3.8.

$$HR_i = C_i / RfC_i \dots\dots\dots (3.8)$$

Where C_i in equation 3.8 is the atmospheric concentration of the VOC species and RfC_i is its estimated maximum acceptable level of exposure by continuous inhalation that has no adverse effects to the human population during the lifetime [44]. RfC_i values were taken from various regulatory boards and have different names in those agencies: Minimum Risk Levels (MRLs) by Agency for Toxic Substances and Disease registry (ATDSR) [45], Reference concentrations (RfC_i) by the EPA Integrated Risk Information System (IRIS) [46], and Reference Exposure Levels (RELs) by the California Office of Environmental Health Hazard Assessment (OEHHA) [47]. Compounds which have no available data from the above agencies were taken from a previous publication [48]. Priority of RfC_i values is based on the most updated data that are available for the

compound. RfC_i values and their sources are summarized in Table 3.2. Cancer risk assessment was carried out by calculating the life time cancer risk (LCR_i) using equation 3.9.

$$LCR_i = C_i \times UR_i \dots \dots \dots (3.9)$$

In equation 3.9, C_i is the concentration of the carcinogen quantified in samples and UR_i is the inhalation unit risk of the cancer-causing agent [44]. UR_i values are provided by the WHO [49], IRIS [46] and OEHHA [47]. The UR_i of a carcinogen is defined as the probability of cancer development in an individual from continuous exposure to the chemical at a concentration of $1 \mu\text{g m}^{-3}$ over a lifespan of 70 years [50]. The source, UR_i value and the International Agency for Research on Cancer (IARC) classification can also be found in Table 3.2. In compliance to the EPA criteria [51], VOC concentrations below the MDL and method quantification limits (MQL) were replaced with half of the MDL and half of the MQL respectively to provide background risk values for unquantifiable VOC amounts.

Table 3.2: Sources and values of Reference concentrations (RfC_i), Unit risks (UR_i) and International Agency for Research on Cancer (IARC) carcinogen classification for target analytes.

Name of Target VOCs	non-cancer reference concentrations RfC_i ($\mu\text{g/m}^3$)	Source of RfC_i	cancer unit risks UR_i ($\mu\text{g/m}^3$)	Source of UR_i	IARC classification
isopropyl alcohol	7300	Chan et al. [48]	-	-	-
hexane	7050		-	-	-
2-butanone	1180		-	-	-
trichloromethane	240		5.30E-06	IRIS	2B
cyclohexane	6000	IRIS	-	-	-
benzene	30	ATSDR	2.90E-05	WHO	1
trichloroethylene	600	OEHHA	2.00E-06	WHO	2A
methyl methacrylate	700	IRIS	-	-	3
methyl isobutyl ketone	3000	IRIS	-	-	-
toluene	300	OEHHA	-	-	3
tetrachloroethylene	40	IRIS	2.60E-07	OEHHA	2A
ethyl benzene	2000	OEHHA	2.50E-06	OEHHA	2B
<i>p, m</i> -xylene	220	ATSDR	-	-	-
styrene	900	OEHHA	-	-	-
<i>o</i> -xylene	220	ATSDR	-	-	3
Phenol	200	OEHHA	-	-	-

3.3 Results and Discussion

3.3.1 Daily Trend Profiles

Daily trend profiles for the 517 samples collected in 5 L volumes were examined. Analysis was conducted for all sampling days that had a complete collection of all 4 intra-day samples. Compounds of interest were categorized according to their functional groups (i.e. hydrocarbons, aromatic compounds and aliphatic carbonyl compounds) to investigate for analogous trend patterns between VOCs that have common functionalities within a particular day. Intra-day concentration graphs were plotted as VOC concentration against the initial time of sampling. For analytes categorized in functional groups, the daily concentration trends were classified into 5 general graph patterns: Trend A, B, C, D and E.

Figure 3.2 shows the graphical description and definition of the 4 different trend types (A to D). In order for categorization to occur, no more than 4 target compounds within the

Figure 3.2: The definition of 4 trend types (Trends A to D) based on the general shapes of daily concentration graphs.

Figure 3.3: Percentage proportion of daily trend profiles following various trend types for analytes categorized according to their functional groups.

functional group for that particular day should deviate from the common trendline. If more than 4 compounds diverge from the common trend pattern, that functional group concentration plot will be classified as trend E, which represents no analogous trend between the graphs plotted for VOCs within the functionality classification. The frequency of common trend occurrence for hydrocarbons, aromatic compounds and aliphatic carbonyl compounds is summarized in Figure 3.3.

The chlorinated compounds of interest do not share an analogous trend for the majority of the intra-day graphs. Thus, individual analysis on the graphs of chlorinated target VOCs was carried out and classified similarly as functional group analysis, into trends A, B, C and D. There is no trend E for chlorinated compounds since individual graphs were analyzed. Individual VOC graph classification was also conducted for ethyl ether and isopropyl alcohol as they are the only target VOCs that exclusively have the ether and alcohol functional group. However, in circumstances where by the VOC concentrations remain consistent throughout the day (i.e. similar in all intra-day samples), the graph is categorized as trend F. Figure 3.4 summarizes the percentage occurrence of each trend for trichloromethane, trichloroethylene, tetrachloroethylene, ethyl ether and isopropyl alcohol.

Figure 3.4: Percentage proportion of daily trend profiles following various trend types for individual analyte analysis.

3.3.1.1 Hydrocarbons and OVOCs

Trend A occurs in 28% of the concentration graphs plotted for aliphatic hydrocarbons and 26% for aromatic hydrocarbons. The amounts of hydrocarbons and aromatic compounds reached the maximum concentration in the air samples collected between 16.22 PM to 19.07 PM. It is very likely that the high VOC concentrations are due to the traffic peak period, where a large number of vehicles are leaving from Tuas and heading eastwards on the PIE. Fuels in motor vehicles were established sources of aliphatic and aromatic hydrocarbons [52-56]. High hydrocarbon emissions (gasoline evaporation or petrol combustion) from vehicle exhaust were due to heavy flow of traffic along the expressway.

Trend B occurs in approximately 36% of the graphs drawn for hydrocarbons and in about 33% of the days for the aromatic analytes. The amounts of these compounds reached the highest concentrations at the unexpected time period between 21.52 PM to 12.37 AM the following day. As there is minimal traffic along the PIE, high amounts of VOCs in the air samples that were collected are believed to be predominantly from nocturnal industrial releases.

Trend C is a common observation for oxygenated volatile organic compounds (OVOCs),

Figure 3.5: The variations of the average temperature and concentration of oxygenated volatile organic compounds (OVOCs) with the starting time of sampling between 2nd February to 15th March 2012.

in which the amounts of OVOCs reached their maximum in samples collected between 10.52 AM to 13.37 PM. 44% of the concentration graphs for aliphatic carbonyl compounds, 31% for ethyl ether and 12% for isopropyl alcohol conformed to Trend C. On the other hand, the minority of the OVOC graphs follow trend A and B. These two observations seem to demonstrate that the OVOCs were predominantly biogenic, since trend A and B were associated with anthropogenic activities. Previous studies have suggested that plants and O_3 would undergo photochemical reactions in the presence of sunlight and higher temperatures to produce C4-C11 saturated aldehydes such as hexanal, heptanal, octanal, nonanal and decanal [57-59]. In addition, naturally-occurring isoprene also reacts with O_3 and hydroxyl (OH) radicals to yield methacrolein [60, 61]. Generations of these carbonyl compounds were found to be dependent on the temperatures and sunlight intensity. Warmer temperatures and intense sunlight would promote the formation of OH radicals from other organic compounds, consequently leading to photolysis and the production of C4-C11 n-alkenals [59]. Figure 3.5 shows the

mean temperature calculated for the sample collection period between 2nd February to 15th March 2012 and the concentration of target aldehydes quantified from samples. The average temperatures and alkenal concentration from 10.52 AM to 13.37 PM were revealed to be the highest. Trend C also recurs in about 12% of the aromatic functional group graphs and 7% for both saturated and non-saturated hydrocarbons. A possible explanation could be due to loss of VOCs via multiple processes in nature such as rain, dry deposition and removal by photolysis [62-64]. Due to the removal of atmospheric VOCs via those pathways, the concentration patterns do not necessarily portray the accurate amount of VOCs that were discharged from anthropogenic sources.

The frequency for trend D for the different functional groups varies. It happens in about 14% for hydrocarbons and 12% for aromatic compounds, but none of the time for aliphatic carbonyls. However, there are still OVOCs that exhibit this trend. From the individual compound analysis, 22% of the isopropyl alcohol graphs mimicked trend D. The highest level of VOCs was reached when sampled between 3.22 AM to 6.07 AM. Since the sampling period is slightly before the peak hour of the expressway, it is likely to be attributed to industrial emissions. Another reason for the observation of trend D could be due to the adsorption of VOCs by precipitation. Rain is a VOC sink and reduces the levels of VOCs present in the air [62, 65, 66].

3.3.1.2 *Chlorinated Species*

Previous studies have identified common biogenic sources and mutually exclusive anthropogenic sources for trichloromethane and trichloroethylene. The soil, the ocean and marine algae are the principle sources of these VOCs [67-69]. Trichloroethylene is utilized as an industrial solvent for degreasing metals, whereas trichloromethane has been used for the manufacturing of paper and pulp, and in water treatment [70, 71]. Based on

comparisons made between the percentage distributions of trichloromethane and trichloroethylene concentration trends (Figure 3.4), it confirms an anthropogenic source contribution for both compounds as they have distinctive differences in their trend profiles. While 28% of the graphs conformed to trend A for trichloromethane, 45% of the graphs plotted for trichloroethylene were classified under the same trend groups. Further supporting evidence was observed from the differences between the trend profiles of tetrachloroethylene and trichloroethylene. Tetrachloroethylene and trichloroethylene share a common industrial source, which is the emission from chemical agents for degreasing metals [72, 73]. Tetrachloroethylene had additional man-made sources, as it is found in the flue gases of coal-fired power stations and in dry cleaning [74, 75]. Dissimilarities in the trend profiles of the second pair of VOCs demonstrated that the emissions were from several sources.

3.3.2 *Monthly Box Plot Analysis*

Based on the monthly concentration box plots for all VOC analytes, it was noted that the maximum VOC concentrations display drastic variations between months. Figure 3.6 shows the monthly box-and-whisker concentration distributions for target analytes 2-butanone and cyclohexane. The box plots for all other compounds of interest can be found in Appendix 2, Figures A2.1 to A2.43. The highest maximum concentration recorded for 2-butanone is $56.43 \mu\text{g m}^{-3}$ while the corresponding value for cyclohexane is $10.60 \mu\text{g m}^{-3}$. As for their monthly averages, the highest readings for 2-butanone and cyclohexane are $6.87 \mu\text{g m}^{-3}$ and $2.25 \mu\text{g m}^{-3}$, respectively. Both compounds registered their highest maximum and average readings in September 2012.

4 other compounds of interest (i.e. 2-ethyltoluene, furfural, methyl methacrylate and trichloroethylene) also have their highest maximum values in September 2012 while 6

Figure 3.6: Monthly box plots for (a) 2-butanone and (b) cyclohexane.

additional VOCs (i.e. 4-ethyltoluene, benzene, methyl methacrylate, decanal, isopropyl alcohol and 3-methylpentane) have their highest monthly mean values in the same month. Another observation made was the general increase in the monthly mean concentration for 36 out of the 46 target VOCs between the period of August 2012 to October 2012. The occurrence of transboundary haze pollution in September 2012 is postulated to be the cause of VOC concentration elevation. The southwest monsoon season typically sets in between June to September each year [76]. The location of the monsoon rain belt was away from Indonesia and this led to severe arid conditions. The situation was worsened by the entrance of Madden-Julian Oscillation dry period, escalating hotspot activities which resulted in the stimulation and dispersion of thick smoke clusters over Southern

Sumatra [77]. Moderate smoke haze generated from hotspot locations resulted in higher average concentrations of certain volatile organic species [78]. PSIs measured in Singapore surged from a value of 40 on 1st September 2012 to a magnitude of 54 on 6th September 2012 and peaked at 68 on 7th September 2012, which was the maximum PSI for 2012 [79].

3.3.3 Overall Annual Statistics

The average, median, maximum, minimum, 25th and 75th percentiles of atmospheric analyte concentrations attained from all samples are summarized in Table 3.3. All %RSD values for the concentrations obtained are $\leq 25\%$. However, for a large dataset (i.e. 517 samples) such as this, the variation between samples is much greater than any error associated with each measurement. The data collected over the span of a year (February 2012 to January 2013) show that the highest maximum concentration registered was from

Table 3.3: Overall concentration statistics (in $\mu\text{g m}^{-3}$) for target VOCs between February 2012 and January 2013.

Name of target analytes	Percentage of concentrations above MQL	average	minimum	25th percentile	median	75th percentile	maximum
isopropyl alcohol	92	3.33	0	0.79	1.60	4.61	29.3
ethyl ether	28	0.77	0	0.07	0.21	0.60	11.0
isoprene	98	2.72	0	0.66	1.67	3.98	20.3
2-methylpentane	97	7.92	<M.D.L.	2.42	5.15	8.38	95.5
methacrolein	96	0.66	0	0.22	0.43	0.75	5.57
3-methylpentane	98	3.13	0	1.16	2.20	4.69	17.2
hexane	95	12.0	<M.D.L.	4.33	8.02	14.6	88.3
2-butanone	90	3.97	0	0.64	1.62	4.50	56.4
trichloromethane	99	0.30	<M.D.L.	0.11	0.17	0.30	10.7
ethyl acetate	99	7.21	0	1.66	3.32	7.03	88.1
methylcyclopentane	100	1.83	<M.D.L.	0.67	1.24	2.56	10.8
cyclohexane	100	1.32	<M.Q.L.	0.41	0.84	1.65	10.6
benzene	96	3.42	<M.D.L.	1.47	2.63	4.51	22.1
heptane	99	1.64	<M.D.L.	0.56	1.15	2.04	13.1
trichloroethylene	96	0.51	0	0.14	0.28	0.59	6.32
methyl methacrylate	49	0.19	0	0	0.06	0.19	3.61
methyl cyclohexane	99	1.18	<M.D.L.	0.28	0.62	1.27	25.9
methyl isobutyl ketone	92	0.76	0	0.19	0.43	0.86	9.42
2-methylheptane	91	0.33	0	0.09	0.19	0.39	5.62
toluene	99	20.4	<M.D.L.	7.98	14.2	27.2	100
1-octene	66	0.30	0	0.00	0.15	0.35	4.84
octane	97	0.53	0	0.18	0.35	0.63	4.97
hexanal	89	0.29	0	0.12	0.21	0.36	3.64
tetrachloroethylene	97	0.37	0	0.09	0.21	0.47	6.15
furfural	16	0.16	0	0	0	0.16	7.89
ethylbenzene	99	5.48	<M.D.L.	1.51	3.40	7.17	58.3
<i>m,p</i> -xylene	98	2.91	<M.D.L.	1.08	2.08	3.76	20.0
nonane	97	0.81	0	0.28	0.54	0.99	8.84

Table 3.3: Overall concentration statistics (in $\mu\text{g m}^{-3}$) for target VOCs between February 2012 and January 2013 (continued).

Name of target analytes	Percentage of concentrations above MQL	average	minimum	25th percentile	median	75th percentile	maximum
heptanal	69	0.24	0	0.04	0.14	0.30	4.06
styrene	99	1.45	<M.D.L.	0.2	0.4	0.76	95.7
<i>o</i> -xylene	99	2.18	<M.D.L.	0.78	1.59	2.94	13.9
phenol	54	0.86	0	0.36	0.63	1.02	6.63
3-ethyltoluene	99	1.07	<M.D.L.	0.32	0.64	1.19	10.9
4-ethyltoluene	81	0.45	0	0.09	0.22	0.44	9.48
benzaldehyde	72	1.05	0	0.26	0.75	1.39	6.99
1,3,5-trimethylbenzene	80	0.48	0	0.1	0.28	0.57	4.85
decane	87	1.13	0	0.34	0.78	1.34	16.2
2-ethyltoluene	94	0.47	0	0.17	0.32	0.58	4.19
octanal	67	0.7	0	0.06	0.26	0.74	17.3
benzonitrile	97	0.39	<M.D.L.	0.12	0.18	0.33	13.6
1,2,4-trimethylbenzene	99	1.75	<M.D.L.	0.61	1.24	2.3	14.8
1,2,3-trimethylbenzene	98	0.48	<M.D.L.	0.15	0.35	0.6	3.28
acetophenone	85	0.66	<M.D.L.	0.29	0.46	0.82	7.87
nonanal	74	1.16	0	0.15	0.62	1.43	14.8
decanal	84	1.9	0	0.33	1.02	2.48	17

toluene at $100 \mu\text{g m}^{-3}$. This is followed by styrene ($95.7 \mu\text{g m}^{-3}$), 2-methylpentane ($95.5 \mu\text{g m}^{-3}$), hexane ($88.3 \mu\text{g m}^{-3}$) and ethyl acetate ($88.1 \mu\text{g m}^{-3}$). Other analytes with maximum concentrations beyond $50 \mu\text{g m}^{-3}$ are 2-butanone and ethylbenzene. Maximum VOC concentrations within the 50 to $100 \mu\text{g m}^{-3}$ range were found in more than 90% of the total samples. As for average concentrations, the highest value was from Toluene ($20.4 \mu\text{g m}^{-3}$) and subsequently in descending order: hexane ($12.0 \mu\text{g m}^{-3}$), 2-methylpentane ($7.92 \mu\text{g m}^{-3}$), ethyl acetate ($7.21 \mu\text{g m}^{-3}$) and ethylbenzene ($5.48 \mu\text{g m}^{-3}$). Several VOCs were identified to be irregular pollutants, quantified in less than 50% of all samples collected. They are ethyl ether (28%), methyl methacrylate (49%) and furfural (16%). Although ethyl ether was not constantly detected in the atmosphere, with only 28% of the total samples having quantified amounts, its maximum concentration reached as high as $11.0 \mu\text{g m}^{-3}$. The 5 most prominent VOCs were compared with their corresponding profiles in other countries. Table 3.4 summarizes the average concentrations of toluene, hexane, ethyl acetate, 2-methylpentane and styrene detected around the world, while Table 3.5 tabulates the available maximum concentration data around the world for the major VOCs.

Table 3.4: Average toluene, hexane, ethyl acetate, 2-methylpentane and styrene concentrations (in $\mu\text{g m}^{-3}$) around the world. “-” represents data not reported for that VOC.

Reference	Country	City	Average concentrations (in $\mu\text{g m}^{-3}$)				
			Toluene	2-methyl pentane	n-hexane	Styrene	ethyl acetate
[80]	S. Korea	Seoul	48.2	4.58	4.69	-	-
[81]	Pakistan	Karachi	26.8	16.6	26.4	-	-
[82]	Thailand	Bangkok	184	-	29.3	-	-
[82]	Philippines	Manila	167	-	9.52	-	-
[83]	Taiwan	Not mentioned	27.5	5.99	2.47	-	-
[84]	Germany	Munich	20.0	4.93	2.11	-	-
[85]	France	Lille	19.3	-	1.76	-	-
[86]	Italy	Rome	99.9	27.4	15.8	-	-
[87]	U.S.A.	Chicago	14.3	8.46	7.05	-	-
[81]	Chile	Santiago	82.2	16.9	14.5	-	-
[88]	China	Jin'an	23.8	-	7.7	-	7.7
	China	Longhu	46.9	-	18.2	-	33.3
	China	Jimei	50.4	-	23.8	-	154
[89]	China	Foshan	41.4	-	8.95	1.15	-
[90]	France	Donon	0.61	0.18	0.14	-	-
[91]	U.K.	London	21.7	6.30	2.2	-	-
[92]	Switzerland	Jungfrauoch	0.10	-	-	-	0.03
[93]	Switzerland	Zurich	5.39	-	-	-	0.68
[23]	Japan	Tokyo (urban)	21.0	-	2.5	0.45	-
	Japan	Tokyo (Roadside)	19.0	-	3.00	0.38	-
[44]	Spain	Catalonia, Tarragona Site 1	2.61	-	1.06	1.25	-
	Spain	Catalonia, Tarragona Site 2	4.26	-	0.39	1.21	-
	Spain	Catalonia, Tarragona Site 3	1.12	-	0.31	0.34	-

Table 3.5: Maximum toluene, hexane and styrene concentrations (in $\mu\text{g m}^{-3}$) around the world. “-” represents data not reported for that VOC.

References	Country	Location	Available Descriptions of Data (Sites/ Season/Time variation)	Toluene	n-hexane	Styrene
[89]	China	Foshan	Foshan Environmental Monitoring Station	185	57.3	6.52
[94]	Turkey	Kocaeli	Middle East Technical University, Environmental Engineering Department	187	-	-
[44]	Spain	Catalonia	Tarragona Site 1	8.30	10.7	4.20
			Tarragona Site 2	26.2	4.80	2.80
			Tarragona Site 3	6.70	7.10	3.70
[95]	Japan	Shizuoka	Summer	11.8	-	-
			Winter	24.2	-	-
[96]	Finland	Helsinki	Outdoor	132	458	6.68
[97]	Spain	Catalonia	Tarragona Site 1	135	-	4.70
			Tarragona Site 2	68.3	-	2.40
			Tarragona Site 3	31.8	-	1.00
			Tarragona Site 4	12.8	-	1.40
			Tarragona Site 5	8.20	-	7.50
			Tarragona Site 6	15.9	-	15.2
			Tarragona Site 7	8.90	-	15.1
[98]	India	Kolkata	New Alipore (Day)	183	-	-
			New Alipore (Night)	123	-	-
			Gariahat (Day)	90.5	-	-
			Gariahat (Night)	37.5	-	-
			Shyambazar (Day)	120	-	-
			Shyambazar (Night)	109	-	-

The maximum toluene concentrations from the western industrial region of Singapore were detected in 3 samples collected on 2nd February 2012 and 28th February 2012 between 16.22 PM to 19.07 PM and 17th April 2012 between 21.52 PM to 12.37 PM. The values are comparable to measurements taken in Graiahat in the day ($90.5 \mu\text{g m}^{-3}$) and Shyambazar at night ($109 \mu\text{g m}^{-3}$), both places are located in Kolkata, India [98]. The average atmospheric levels of toluene found in the western industrialized region of Singapore are similar to those quantified in Jin'an, Fuzhou ($23.8 \mu\text{g m}^{-3}$) in China during the winter season [88]. The value is also close to concentrations detected in London, United Kingdom ($21.7 \mu\text{g m}^{-3}$), Tokyo, Japan ($19\text{-}21 \mu\text{g m}^{-3}$), Munich, Germany ($20.0 \mu\text{g m}^{-3}$) and Lille, France ($19.3 \mu\text{g m}^{-3}$) [23, 84, 85, 91]. When compared to the average concentrations present in neighboring Southeast Asian countries, the average toluene emissions in Singapore are about 11% to 12% the mean toluene concentrations in Bangkok, Thailand ($184 \mu\text{g m}^{-3}$) and Manila, The Philippines ($167 \mu\text{g m}^{-3}$) [82].

High maximum readings for 2-methylpentane and ethyl acetate were measured: $95.5 \mu\text{g m}^{-3}$ and $88.1 \mu\text{g m}^{-3}$, respectively at the sampling site. Unfortunately, maximum data were not readily available or reported in several publications. Hence, comparisons were performed for the average measurements of these compounds. The mean for 2-methylpentane ($7.92 \mu\text{g m}^{-3}$) was comparable to the average measurements in London, United Kingdom ($6.30 \mu\text{g m}^{-3}$) and Chicago, USA ($8.46 \mu\text{g m}^{-3}$) [87, 91]. It is about 0.5 times the average concentration in Karachi, Pakistan ($16.6 \mu\text{g m}^{-3}$) but 44 times higher than the amounts in Donon, France ($0.18 \mu\text{g m}^{-3}$) [81, 90]. As for ethyl acetate, its average of $7.21 \mu\text{g m}^{-3}$ is only 5% of the mean concentration taken in the Jimei district in Xiamen, China [88]. But when compared with the summer values in Zurich and Jungfrauoch, both in Switzerland, it is approximately 10 times and 240 times higher, respectively [92, 93].

The maximum hexane concentration in western Singapore, at $88.3 \mu\text{g m}^{-3}$, was detected in the sample obtained on 12th December 2012 between 16.22 PM to 19.07 PM. The value lies between the maximum concentrations measured in one of the sites in Catalonia, Spain ($4.80 \mu\text{g m}^{-3}$) and Helsinki, Finland ($458 \mu\text{g m}^{-3}$) [96, 97]. Its average amounts are in comparison with those detected in Santiago, Chile ($14.5 \mu\text{g m}^{-3}$) and Rome, Italy ($15.8 \mu\text{g m}^{-3}$) but much higher than other countries in Asia such as Seoul, South Korea ($4.69 \mu\text{g m}^{-3}$) and Taiwan ($2.47 \mu\text{g m}^{-3}$) [80, 81, 83, 86].

Styrene has the highest maximum reading after toluene at $95.7 \mu\text{g m}^{-3}$. On the global scale, it is much higher than the few reported studies from Foshan, China ($6.52 \mu\text{g m}^{-3}$), Catalonia, Spain ($1\text{-}15.2 \mu\text{g m}^{-3}$) and Helsinki, Finland ($6.68 \mu\text{g m}^{-3}$) [89, 96, 97]. The average measurement ($1.45 \mu\text{g m}^{-3}$), on the contrary, is similar to values from Foshan, China ($1.15 \mu\text{g m}^{-3}$) and Catalonia, Spain ($1.21\text{-}1.25 \mu\text{g m}^{-3}$) [44, 89].

3.3.4 Source Apportionment

The similar shapes of the concentration graphs between various alkanes and aromatic compounds indicate that they may be coming from similar sources. Correlation investigations were implemented on the dataset to estimate the possible mutually common and exclusive sources of these VOCs. PMF modeling was used to determine the number of sources and the VOC mass fraction distributions from each source.

3.3.4.1 Spearman Correlations and Coefficients of Determinations

A total of 28 pairs of VOCs were found to have strong positive and negative Spearman coefficients of $\rho \geq 0.8$ or $\rho \leq -0.8$. The ρ coefficients for each VOC pairs are listed in Table 3.6. Two pairs of OVOCs were shown to have $\rho \leq -0.8$ and they are between: (i) methyl methacrylate and ethyl ether, and (ii) nonanal and furfural. The generation of one

OVOC in the atmosphere seems to result in the removal of the other. 26 hydrocarbon pairs were revealed to have $\rho \geq 0.8$. Positive monotonic relationships between these hydrocarbons seem to suggest mutually common sources. 3 pairs of hydrocarbons have coefficients of determinations (R^2) of at least 0.8. The correlation plots for the 3 pairs of hydrocarbons are depicted in Figure 3.7. The R^2 value between 3-methylpentane and methylcyclopentane is 0.8512, indicating that 85% of the variation in methylcyclopentane was accounted for by the variation in 3-methylpentane. This also means that 85% of the explained variation for the hydrocarbon pairs was due to common sources such as

Table 3.6: VOC pairs and their corresponding Spearman coefficient values.

VOC pairs with $\rho \geq 0.8$ or $\rho \leq -0.8$		ρ
methylcyclopentane	3-methylpentane	0.88
heptane	cyclohexane	0.85
methylmethacrylate	ethyl ether	-0.82
methylcyclohexane	cyclohexane	0.83
methylcyclohexane	heptane	0.83
octane	cyclohexane	0.82
octane	heptane	0.83
m,p-xylene	ethylbenzene	0.91
nonane	octane	0.80
o-xylene	cyclohexane	0.81
o-xylene	heptane	0.81
o-xylene	methylcyclohexane	0.80
o-xylene	ethylbenzene	0.90
o-xylene	m,p-xylene	0.97
3-ethyltoluene	m,p-xylene	0.85
decane	nonane	0.80
2-ethyltoluene	m,p-xylene	0.83
2-ethyltoluene	3-ethyltoluene	0.87
1,2,4-trimethylbenzene	methylcyclohexane	0.80
1,2,4-trimethylbenzene	m,p-xylene	0.90
1,2,4-trimethylbenzene	3-ethyltoluene	0.94
1,2,4-trimethylbenzene	2-ethyltoluene	0.91
1,2,3-trimethylbenzene	ethylbenzene	0.81
1,2,3-trimethylbenzene	m,p-xylene	0.85
1,2,3-trimethylbenzene	3-ethyltoluene	0.86
1,2,3-trimethylbenzene	2-ethyltoluene	0.86
1,2,3-trimethylbenzene	1,2,4-trimethylbenzene	0.92
nonanal	furfural	-0.84

Figure 3.7: Correlation graphs plotted between VOCs with R^2 coefficients above 0.8.

automobile emissions and petroleum-associated industries, while the other 15% of the unexplained variation was due to separate sources. The two compounds are used for other industrial applications and this could attribute to the unexplained variations. Methylcyclopentane is an important benzene precursor in aromatic production plants and is used to generate benzene [99, 100]. 3-methylpentane, on the other hand, is used in glues for shoe manufacturing [101].

1 pair of hydrocarbons that had $R^2 > 0.8$ were aromatic isomers. Mutual sources between *m,p*-xylene and *o*-xylene result in a high coefficient of determination. For instance, all xylenes are emitted from vehicle exhausts, together with benzene, toluene and ethylbenzene [88, 102]. They are also generated from aromatic process industries in which toluene is utilized as a feedstock or acquired from fractional distillation of petroleum [103, 104]. 92% of the variation in *m,p*-xylene can be explained by the variation in *o*-xylene, and could be associated with the source suggestions made above. The other 8% of unexplained variation were related to exclusive sources that are unique to each organic compound. *p*-xylene is a feedstock for manufacturing purified terephthalic acid that is used in the production of fibre and plastic bottles, while *o*-xylene is a raw material for alkaline resins and plasticizers [105, 106].

A high coefficient of determination was also noted between 1,2,4-trimethylbenzene and *o*-xylene. 81% of the variations in 1,2,4-trimethylbenzene is related to the variations in *o*-xylene. Both aromatic compounds are found in the gasoline constituent of crude oil during fractional distillation and catalytic reforming [107, 108]. The mentioned proportions of explained variations also correspond to other common sources such as solvents in paint coatings and thinners [109]. Unaccountable variations were associated to dissimilar sources such as 1,2,4-trimethylbenzene required in the manufacturing of dyes,

Figure 3.8: Percentage contribution of VOCs for each PMF source profile.

m^{-3} , 23%), benzene ($1.11 \mu\text{g m}^{-3}$, 43%), ethylbenzene ($0.774 \mu\text{g m}^{-3}$, 17%) and toluene ($7.59 \mu\text{g m}^{-3}$, 51%). Considerable amounts of xylene isomers (*m,p*-xylene- $0.729 \mu\text{g m}^{-3}$, 30% ; *o*-xylene- $0.533 \mu\text{g m}^{-3}$, 29%), and trimethylbenzene isomers (1,2,4-trimethylbenzene- $0.456 \mu\text{g m}^{-3}$, 32% and 1,2,3-trimethylbenzene- $0.0678 \mu\text{g m}^{-3}$, 17%) were also present. 66% of styrene was also contributed from this source. The typical markers such as ethane, ethylene, isobutene and n-butane for fingerprinting oil refinery sources were not evaluated in this study, thus the patterns for the compounds that were discussed were matched to petroleum-related profiles. Factor 2 matched well to the source profile attained for crude oil refineries in earlier investigations [38-40].

Factor 3 is related to biogenic and secondary VOCs as it contains high amounts of isoprene ($2.08 \mu\text{g m}^{-3}$, 86%). The presence of toluene ($0.630 \mu\text{g m}^{-3}$, 4%) and hydrocarbons such as hexane ($0.841 \mu\text{g m}^{-3}$, 10%), 3-methylpentane ($0.154 \mu\text{g m}^{-3}$, 6%) and 2-methylpentane ($0.245 \mu\text{g m}^{-3}$, 5%) implies that the source is not completely due to

the natural environment since it comprises of anthropogenic VOCs such as toluene and isomers of hexane. The sampling site is quite unique due to its semi-urban surroundings. The proximity of the university campus consists of an expressway and several factories to the south and a forest in the north-west direction which is used for occasional military exercises. Thus, the air quality under normal circumstances is predicted to be partially urban and rural.

High amounts of 2-methylpentane ($0.884 \mu\text{g m}^{-3}$, 18%), benzene ($0.788 \mu\text{g m}^{-3}$, 31%) and heptane ($0.721 \mu\text{g m}^{-3}$, 59%) were observed in factor 4. This factor also contributed 82% of 1-octene and 59% of octane. The percentage contributions of the mentioned hydrocarbons matched very well with the evaporative emissions source profile obtained from a publication [38] even though the marker compounds for the source are C4 hydrocarbons which are not analyzed in this work.

Factor 5 is linked to emissions from transportation on the roads. It is predominantly enriched with toluene ($0.769 \mu\text{g m}^{-3}$, 5%), ethylbenzene ($0.139 \mu\text{g m}^{-3}$, 3%), *m,p*-xylene ($0.411 \mu\text{g m}^{-3}$, 17%) *o*-xylene ($0.326 \mu\text{g m}^{-3}$, 18%), 1,2,4-trimethylbenzene ($0.530 \mu\text{g m}^{-3}$, 37%), 2-methylpentane ($0.140 \mu\text{g m}^{-3}$, 3%), 3-ethyltoluene ($0.283 \mu\text{g m}^{-3}$, 41%), 4-ethyltoluene ($0.163 \mu\text{g m}^{-3}$, 68%), 2-ethyltoluene ($0.221 \mu\text{g m}^{-3}$, 60%), 1,3,5-trimethylbenzene ($0.229 \mu\text{g m}^{-3}$, 91%) and 1,2,3-trimethylbenzene ($0.163 \mu\text{g m}^{-3}$, 41%). Substantial amounts of benzene ($0.0431 \mu\text{g m}^{-3}$, 2%), cyclohexane ($0.0196 \mu\text{g m}^{-3}$, 2%), heptane ($0.0435 \mu\text{g m}^{-3}$, 4%) and 1-octene ($0.0356 \mu\text{g m}^{-3}$, 14%) were also observed. To decide whether factor 2 or factor 5 is from automobiles or oil refineries, all ethyltoluene isomers are utilized as a collective indicator since they are exclusively present in vehicular exhausts according to previous studies [38, 39, 113]. Factor 5 is verified to be vehicular in origin since all ethyltoluene isomers are found in this profile.

Factor 6 was characterized by the large quantities of C6 and C7 hydrocarbons [i.e. 2-methylpentane ($2.61 \mu\text{g m}^{-3}$, 52%), 3-methylpentane ($1.38 \mu\text{g m}^{-3}$, 58%), hexane ($7.23 \mu\text{g m}^{-3}$, 83%), methylcyclopentane ($0.927 \mu\text{g m}^{-3}$, 67%), cyclohexane ($0.194 \mu\text{g m}^{-3}$, 21%) and heptane ($0.102 \mu\text{g m}^{-3}$, 8%), with trace amounts of aromatics and higher hydrocarbons above 8 carbons. The marker compounds of the source strongly imply that the factor is attributed to emissions from consumer and households, based on the source profile acquired from a previous study [75].

The major component in factor 7 is nonane ($0.379 \mu\text{g m}^{-3}$, 59%) and decane ($0.611 \mu\text{g m}^{-3}$, 78%). The high amounts and percentage contributions of C9 and C10 hydrocarbons indicates that this factor is a source for industrial coatings [38].

3.3.5 Non-Cancer Risk Assessment

16 of the 46 volatile organic analytes have reference concentrations that were available from various databases and the non-cancer effects for these compounds were investigated.

HR_i values for the quantified amounts of those 16 compounds were calculated and are

Figure 3.9: HR_i box plots for 16 VOCs with known RfC_i . The orange and red line represents the level of potential concern ($HR_i = 0.1$) and the level of concern ($HR_i = 1$) respectively.

represented in the box and whisker diagrams shown in Figure 3.9. $HR_i > 1$ indicate that the non-cancer effects for the compound have reached a level of concern, whereas HR_i between 0.1 and 1 signify that the non-cancer effects for the compound is of potential concern [115]. Benzene has the highest HR_i for non-cancer effects, followed by toluene. The average HR_i value for benzene is 0.112, which is above the potential concern level. Although none of the HR_i values for benzene reached the level of concern (i.e. $HR_i > 1$), the percentage of HR_i values that are above the level of potential concern (i.e. $HR_i > 0.1$) is 44%. 22% of the HR_i values of toluene are of potential concern and have ratio values above 0.1. Other compounds that have ratios above 0.1 are tetrachloroethylene (0.27% of the samples) and styrene (0.08% of the samples), but in very low numbers of samples.

3.3.6 Cancer Risk Assessment

5 target VOCs (i.e. benzene, ethylbenzene, chloroform, trichloroethylene and tetrachloroethylene) were calculated for LCR_i based on the existing cancer UR_i values accessible from different databases. Figure 3.10 shows the box and whisker diagram of the LCR_i values calculated for those compounds. A LCR_i of 10^{-6} is defined as 1 case of

Figure 3.10: LCR_i box plots for 5 target carcinogens with known UR_i values (left). The red line represents an LCR_i of 10^{-4} (definite risk). On the right, the zoomed-in version of the LCR_i box plots with the yellow and orange line representing LCR_i values of 10^{-6} (possible risk) and 10^{-5} (probable risk) respectively.

cancer development per 1,000,000 people due to exposure from the environment. That value was taken as a reference as suggested by the EPA [116]. Compounds with LCR_i values above 10^{-6} are interpreted as a “possible risk” whereas those between 10^{-5} and 10^{-4} are described as a “probable risk”. Values that are beyond 10^{-4} represent a “definite risk”. The ranges of values for interpreting different levels of risk were adapted from a previous publication [117].

In acquiescence to a previous health risk assessment study that was conducted, compounds were classified into groups based on (i) their frequency of detection with a known value (15% as a reference percentage requirement) and (ii) their average LCR_i (using 10^{-6} as a reference LCR_i value) [44]. All compounds that were measured are present in >15% of all samples acquired. Benzene and trichloroethylene were quantified in 96% of the samples while trichloromethane, tetrachloroethylene and ethylbenzene were measured in 99% of the samples. Therefore, the impact of replacing immeasurable concentrations with half of the MDLs is very minimal on the LCR_i readings for all 5 VOCs. Group A compounds contains trichloromethane, benzene and ethylbenzene. All of which have average values above 10^{-6} . Group B contains trichloroethylene and tetrachloroethylene, since the average LCR_i values for the compounds are beneath 10^{-6} .

Benzene, an IARC group 1 carcinogen, has the highest LCR_i average in group A, as well as for all 5 target analytes. Its mean LCR_i is 9.72×10^{-5} which indicates a probable risk in cancer development of 9.72 new cases per 100,000 people, assuming the sampling site and the residential area are subjected to the same amount of exposure. 37% of the LCR_i values obtained for the concentration of benzene in the samples collected over a year are above 10^{-4} and of definite risk of developing cancer. The maximum LCR_i for benzene is 6.41×10^{-4} , which represents 6.41 additional cases in 10,000 people. All benzene LCR_i s

are above the “possible risk” values of 10^{-6} .

Ethylbenzene has the second highest LCR_i average of 1.36×10^{-5} , which suggests a probable risk of 1.36 new cases in 100,000 people. 0.14% of the ethylbenzene LCR_i s are above the “definite risk” value of 10^{-4} and 42% of LCR_i have a “probable risk” range between 10^{-4} and 10^{-5} . Trichloromethane has a mean LCR_i of 1.56×10^{-6} , which is within the range of the “possible risk”, between 10^{-5} and 10^{-6} . 44% of the trichloromethane LCR_i s falls above the “possible risk” region.

In Group B, although trichloroethylene and tetrachloroethylene have average LCR_i s below 10^{-6} (i.e. 9.90×10^{-7} and 9.58×10^{-8} correspondingly), it was noted that both compounds have a certain proportion of their LCR_i values exceeding 10^{-6} . 29% of the trichloroethylene LCR_i s and 0.29% of the tetrachloroethylene LCR_i s were above the “possible risk” value as shown in Figure 3.10. They are beyond the yellow line which represents the 10^{-6} value.

Based on the risk assessment conducted for cancer effects, it was observed that continuous exposure to high concentrations of atmospheric VOCs can have serious and harmful consequences to public health. Since only 5 of 46 target compounds were investigated for their effects, further studies should be performed to determine the UR_i values for more VOCs, so that similar cancer risk evaluations can be conducted for other probable or possible carcinogens in IARC. From Table 3.2, several target VOCs that have probable and possible carcinogenic effects on humans are Styrene (IARC Group 2B), phenol (IARC Group 3), methyl methacrylate (IARC Group 3) and xylene isomers (IARC Group 3).

3.3.7 *Uncertainties of the Risk Assessment*

Several uncertainties and limitations exist in the health risk analysis carried out in previous sections. First and foremost, the selection of the analytical method could tremendously impact the accuracy of the quantitative risk assessment. This is because the risk calculation, which is dependent on the VOC concentration obtained from the analytical method, is highly reliant on the method's sensitivity. Lower detection and quantification limits enhance the analytical procedure performance and enable the precise determination of lower VOC amounts as well as the identity of unconventional VOCs present in ultra-low quantities. Liquid extraction (LE) and thermal desorption (TD) are the two principle analytical techniques coupled with GCMS utilized for quantitative monitoring of atmospheric VOCs [118]. A comparison was made between the two methods in previous studies and has shown that TD-GCMS is a more sensitive than Liquid Extraction Gas Chromatography Mass Spectrometry (LE-GCMS). Hence, uncertainties and limitations were minimized in terms of the sensitivity of the analytical procedure.

Another limiting factor is that RfC_i values were not standardized between different health and environmental agencies. More research and studies are required to obtain a comparative value for the different VOCs between agencies. In addition to standardization, it was noted that not all VOCs have established RfC_i and UR_i values. Only 16 of the 46 compounds were analyzed for non-cancer effects and 5 of the 46 compounds were analyzed for cancer effects. Nevertheless, quantitative risk analysis is still a useful indicator for the harmful impact on public health. Simple calculated HR_i s and LCR_i values are good estimates for evaluating the condition of the environment and its harmful effects to human beings.

3.4 Conclusion

Regular monitoring of 46 atmospheric VOC pollutants was performed for a one year period between February 2012 and January 2013. A total of 517 samples were acquired and the VOC concentration measurements were evaluated using different statistical calculations and risk assessment analysis. The possible effects of environmental conditions on the fate of atmospheric VOCs were accounted and the impact of certain VOC concentrations on public health was determined. Spearman coefficients, coefficients of determination and PMF 3.0 modeling were carried out to determine the source profiles and concentration proportions associated to each source.

Intra-day trend profiles from 5 L samples approximated that more than 50% of the daily concentration patterns for hydrocarbons were associated with anthropogenic sources based on geographical information of the sampling site and the traffic situation on the expressway at varying times of the day. About half of the daily trends were related to man-made activities were from vehicular emissions while the other half were associated with industrial processes such as crude oil refining, chemical manufacturing and incineration facilities. Certain amounts of OVOCs, on the contrary, were possibly biogenic as 44% of the graph trends record maximum concentrations in samples acquired in the morning to early afternoon where the average temperature and sunlight intensity were the highest. The high yield of alkenals is likely to be attributed from photochemical reactions between plants and OH radicals [57-59]. Overall annual statistics calculated for all analytes reveal that high abundance of toluene, 2-methylpentane, hexane, ethyl acetate and styrene are present in the atmosphere. Toluene has the highest maximum concentration at $100 \mu\text{g m}^{-3}$, which is similar to concentrations found in Kolkata, India [98]. The overall average level for toluene is comparable to Tokyo, Lille, London and

Munich but is only about 12% of the average toluene concentration in Thailand and The Philippines [23, 82, 84, 85, 91].

Monthly box and whisker analysis show that 8 VOCs (i.e. 2-butanone, 4-ethyltoluene, benzene, cyclohexane, methyl methacrylate, decanal, isopropyl alcohol and 3-methylpentane) have the highest mean in September 2012 and 36 VOCs exhibited increments in average concentrations between August to October 2012. 6 VOCs (i.e. 2-butanone, cyclohexane, 2-ethyltoluene, furfural, methyl methacrylate and trichloroethylene) recorded their highest monthly maximas in September 2012. Concentration spikes in monthly average or maximums were possibly due to the haze caused by Sumatran forest fires that were transported over Singapore by the southwest monsoon winds in September 2012 [119].

Strong Spearman coefficients of $\rho \geq 0.8$ and $\rho \leq -0.8$ were found between 26 pairs of hydrocarbons and 2 pairs of OVOCs respectively. 3 pairs of hydrocarbons have R^2 coefficients ≥ 0.8 . 1 out of the 3 hydrocarbon pairs was a pair of aromatic isomers. The explained variations were connected to common sources between the VOC pairs such as automobile exhausts and industrial emissions, while the unaccountable variations were due to mutually exclusive sources such as dye, perfume and pharmaceutical production. PMF modeling confirmed 7 source profiles for the modeled VOCs.

Health risk assessment was carried out for non-carcinogenic and carcinogenic effects. 16 VOCs were investigated for their non-cancer hazards by calculating HR_i s, while 5 carcinogens were examined for their cancerous effects by calculating the LCR_i s for all concentrations found in samples. Benzene has the highest average HR_i (0.112) and LCR_i (9.72×10^{-5}). 44% of benzene HR_i s were above the potential level of concern. 37% of

benzene LCR_i s are above the definite risk of 10^{-4} and the maximum LCR_i obtained reach as high as 6.41×10^{-4} .

Uncertainties and limitations in the health risk assessment were due to missing information for the calculations of HR_i s and LCR_i s for 30 compounds of interest. Extensive research is required for standardizing reference concentrations and cancer unit risks between environmental and toxicological agencies, as well as for expansion of databases of RfC_i and cancer UR_i s for a wider range of VOCs.

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Sorbent Properties of Carbon Nanotubes and its Derivatives for Thermal Desorption Gas Chromatography Mass Spectrometry Analytical Applications

4.1 Introduction

VOCs are a group of environmental pollutants that have been comprehensively studied for decades. However, protocols for analyzing this class of contaminants are not always well-established or regulated due to their complicated formation and degradation cycle in the environment. Advancement and progress in technology is essential to understand the complexities of their fate in the atmosphere. Enhancements in analytical techniques for sampling accurate quantities of VOCs thus become very important for finding key information about them.

Sorbent-based sampling coupled with TD-GCMS is a well-established approach for monitoring and analysis of an extensive range of atmospheric VOCs due to its high sensitivity, reliability and low detection limits [1]. The sorbent performs as a trap for VOC analytes before desorption via high temperature heating. Some of the important sorbent material characteristics required for the application are thermal stability and high adsorption and desorption efficiency of organic species of interest [2]. There are several existing limitations in the current commercially available sorbents that are used for thermal desorption, such as porous polymers, graphitized carbon black and molecular sieves. Disadvantages of the conventional materials include limited thermal cycles,

temperature constraints, presence of artifacts that interfere with trace level quantification and inability to trap a wide range of compounds in one sorbent material [3, 4]. Carbon nanotubes (CNTs) have captured the interest of the scientific community since their discovery in 1991 [5]. Extraordinary physical properties of CNTs such as thermal stability, high aspect ratios, nano-scale dimensions and mechanical strength have been exploited for several practical applications in analytical research such as biosensors, voltammetry and chromatography [6-9]. CNTs can be categorized into 2 main types: multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). The primary difference in their structures is the number of graphene sheets (sp^2 carbon), encircled around a central core to form the tube structure. The cylindrical tube is composed of numerous graphene sheets in MWCNTs and only a single graphene sheet in SWCNTs. Adsorption of organic species on CNTs involve non-covalent interactions on the exterior surfaces and in the interstitial gaps [10]. Alterations and derivatizations can be made to these well-defined hydrophobic structures to enhance their capabilities for various analytical applications and for improvement to system stability and specificity [11]. The potential of CNTs as superior sorbent materials have been displayed in numerous scientific studies. Long et al. have reported CNTs to be excellent for the removal of toxic dioxin in the environment [12]. Lattore and coworkers worked with a CNT-packed micro-column for preconcentrating metals for atomic spectrometric methods [13]. Liang and colleagues utilized MWCNT as a sorption substrate in solid-phase extraction [14]. Li and Yuan have investigated CNTs performance as a stationary phase in chromatographic analysis [15].

There are several reports of CNT sorbents supported on silica gel to prevent agglomeration that could cause non-uniform packing in the tube and poorer recoveries of certain VOCs [16, 17]. However, silica gel is not an ideal support for sorbent sampling in

an environment with high relative humidity due to its hydrophilicity. These studies have reported on the effects of relative humidity for only 9 non-polar VOCs [16, 17]. Existing literature on the utilization of non-supported CNTs as TD-GCMS sorbents, include MWCNT incorporated together with a conventional sorbent material to form a multi-sorbent tube for analysis, and SWCNT that were evaluated for 10 VOCs [18, 19]. This study aims to explore and contrast the potential of MWCNT, carboxylated MWCNT (COOH-MWCNT), SWCNT, short-length SWCNT (sSWCNT) and carboxylated SWCNT (COOH-SWCNT) as effective sorbent materials for the trapping of 48 atmospheric VOC analytes using solution injection method coupled with TD-GCMS. Previous publications have reported the loading of gas phase standards into the sorbent tube for analyzing the desorption recoveries [16-19]. In this study, the viability of standard solutions was evaluated. The loading method for injecting compounds of interest into traditional sorbent tubes using methanol as a solvent through a calibration loading rig was employed in this study. Because previous publications [16, 18] had reported on the adsorption of methanol on MWCNT, the influence of the solvent for transporting analytes to the CNT surfaces was determined in this study.

4.2 Experimental

4.2.1 Materials and Chemicals

All CNTs (Nanostructured and Amorphous Materials Inc, Texas, USA) were purchased and synthesized by catalytic chemical vapor deposition (CVD). Each sorbent material was packed into separate individual sorbent tubes with dimensions 89 mm $\times$ 6.4 mm o.d (Markes International Limited, Llantrisant, U.K). The mass packed for MWCNT and COOH-MWCNT was 100 mg, whereas the mass packed for SWCNT, COOH-SWCNT and sSWCNT was 75 mg. sSWCNT was used for the investigation of the effects of CNT

length on the desorption recoveries of VOCs. Only 75 mg was packed for the different types of SWCNTs due to space restrictions of the tubes and the flocculated nature of the materials.

Both types of MWCNT have the following dimensions: outer diameters between 50-80 nm, inner diameters within 5-15 nm, 10-20 μm in length with surface areas of 60-80 m^2/g and 95% in purity. COOH-MWCNT contains 0.47-0.51 wt% $-\text{COOH}$ groups after derivatization. SWCNT and COOH-SWCNT were both 1-2 nm in diameter, 5-30 μm in length, have surface areas between 300-380 m^2/g with > 95% CNT purity and > 90% SWCNT purity. COOH-SWCNT has 2.59-2.87 wt% of $-\text{COOH}$ functionalization. sSWCNT has majority of its properties identical to SWCNTs mentioned above (i.e. diameters between 1-2 nm, surface areas between 300-380 m^2/g with > 95% CNT purity and > 90% SWCNT purity) except for its length, which ranged between 1-3 μm .

Conventional multi-sorbent tubes pre-packed with 200 mg Tenax TA and 100 mg Carboxen 100 (Markes International Limited, Llantrisant, U.K) were used as a reference for nano-sorbent tubes. Before their first use, they were conditioned at 320 $^{\circ}\text{C}$ for 2 hours followed by 335 $^{\circ}\text{C}$ for 30 minutes. The conditioning method for subsequent usage of those tubes was at 320 $^{\circ}\text{C}$ for 1 hour. Conditioning of all nano sorbent tubes and conventional sorbent tubes were carried out in the automated tube conditioner TC-20 (Markes International Limited, Llantrisant, U.K) using a nitrogen flow of 70 mL/min.

48 VOCs that were regularly detected in the ambient air in Singapore were purchased from Sigma Aldrich (St Louis, USA), Fluka (Buchs, Switzerland), Alfa Aesar (Heysham, Lancashire, UK), Acros Organics (Geel, Belgium) and Merck (Hohenbrunn, Germany). VOC standard solutions for analysis were produced via dilution of these neat chemicals. Methanol (Schedelco, Malaysia) was chosen as the medium of solvation since it does not

retain on conventional sorbent surfaces but was suggested to have strong adsorption and desorption on CNTs [16, 18]. The effects and feasibility of methanol for injection of standards into the different CNTs were investigated. The preparation of each VOC stock solution (20% v/v) was carried out by pipetting 1 mL of neat chemical into a 5 mL volumetric flask, topped up and homogenized using methanol (Schedelco, Malaysia). This was followed by the formation of individual 50 g/L VOC solutions derived from the stock solutions. Lastly, 500 μ L of individual 50 g/L VOC solutions were added into a 50 mL volumetric flask and dissolved with methanol. This final solution in the 50 mL volumetric flask was the 500 ng/ μ L VOC standards mixture employed for sorbent tube experiments conducted in this study. A fresh 500 ng/ μ L VOC standards mixture was prepared weekly and stored at 4 °C in darkness.

4.2.2 Instrumentation

4.2.2.1 Sorbent Tube Experiments

An Ultra TD-100 Autosampler (Markes International Limited, Llantrisant, U.K) and an UNITY Series 2 (Markes International Limited, Llantrisant, U.K) were utilized together for this study. The Ultra TD-100 was employed for automated transportation of sorbent tubes into the primary desorption compartment, which is linked to the secondary desorption chamber consisting of an electrically-cooled cold trap that is held at -10 °C. During the first stage, sorbent tubes were heated (i.e. 375 °C for nano sorbent tubes and 280 °C for Tenax/Carbopack X multi-sorbent tubes) for a period of 10 minutes. The desorbed analytes were transported to the hydrophobic Tenax cold trap via helium carrier gas (99.999% purity) at 45 mL/min, moving through the sorbent tube. The step was conducted using splitless mode for complete transfer of VOCs onto the trap. The second stage occurred by elevating the temperature of the cold trap to 300 °C instantly and

simultaneously altering the direction of the helium flow. Organic species preconcentrated on the cold trap were desorbed from the cold trap for 7 minutes with a split flow of 6 mL/min, directed to an Agilent 7890A GC (Agilent Technologies, USA).

An Agilent J & W DB-VRX (122-1564 260 °C 60 m × 250 µm × 1.4 µm) column was used for separation of compounds and the mobile phase carrier gas was 99.999% helium at a flow of 1.5 mL/min. The GC oven temperature program was set at 30 °C for 12 minutes, raised to 60 °C at 30 °C/min and subsequently elevated to 124 °C at 40 °C/min. The oven was kept at 124 °C for 2 minutes, prior to another temperature increment to 200 °C at a rate of 9 °C/min. The oven temperature remained constant at 200 °C for 3 minutes. The separated VOC components were evaluated by an Agilent Inert 5975C MS using 70 eV electron impact ionization. The temperature of the ion source was applied at 230 °C, while the quadrupole mass analyzer temperature was set at 150 °C. Scan mode was employed for a mass range of 35-300 amu.

4.2.2.2 *CNTs Characterization Experiments*

Thermogravimetric analysis (TGA) on the CNTs was performed using a Thermogravimetric Analyzer Q500 (TA Instruments, North America) to investigate their degradation temperatures. A sample of CNT material was loaded onto a platinum pan which was placed into the furnace under an atmosphere of nitrogen. The platinum pan in the furnace was originally heated to 150 °C for 30 minutes to eliminate water in the material. The temperature was then increased to 950 °C at a temperature ramp rate of 10 °C/min. Another TGA experiment was performed to monitor the effects of extended heating at 380 °C for all CNTs, which is the maximum operating temperature of the TC-20 thermal conditioning equipment (Markes International Limited, Llantrisant, U.K). The CNT-filled pan was introduced into the furnace and heated to 150 °C for 30 minutes to

vaporize all moisture in the sample and subsequently raised to 380 °C at a rate of 19 °C/min. The period of heating at 380 °C was 20 hours for MWCNTs and SWCNT, and 17 hours for COOH- SWCNT and sSWCNT.

Confocal Raman spectra data were acquired by using a LabRAM HR (Horiba Jobin Yvon, Japan). All measurements were conducted using a HeNe laser excitation at a wavelength of 633 nm. A programmable 1600 W microwave digester (MARS 5, CEM Corp., Matthews, NC, USA) and Easy Prep Teflon-lined vessels (MARS 5, CEM Corp., Matthews, NC, USA) were employed for the closed vessel digestion of CNTs to determine their elemental impurities. External ESP-1500 Plus and RTP-300 Plus sensors were utilized for the inspection of pressure and temperature respectively, in the vessel. 50 mg of CNTs were weighed into the Teflon vessels and 3 mL of ultrapure nitric acid (Avantor™ Performance Materials, Inc., Canada) was added. Filtration of residual particles from the digested solution was carried out using a 0.45 µm polyethersulfone filter (Sartorius stedim biotech S.A., Goettingen, Germany) and diluted to 50 mL. The temperature program for microwave digestion was set to ramp to 185 °C in 20 minutes and was maintained at that temperature for an additional 15 minutes. Concentration of the elements in the digested CNT solution was obtained using an Agilent 7700 series inductively coupled plasma mass spectrometry (ICPMS) (Agilent Technologies, Japan) coupled with a 3rd generation He reaction/collision cell (ORS3) to reduce interferences.

4.3 Results and Discussion

4.3.1 CNTs Characterization Experiments

4.3.1.1 TGA

As high temperature heating is essential for desorption of trapped analytes on the nano-

Figure 4.1: TGA thermograms for (a) MWCNT and COOH-MWCNT (b) SWCNT, COOH-SWCNT and sSWCNT.

sorbent surfaces in TD-GCMS, it is important to investigate the degradation temperatures of all CNTs to prevent overheating and degradation of the materials during analysis. The thermograms of the nanomaterial provide the decomposition temperatures of each type of CNT in an inert atmosphere of nitrogen.

From the TGA results in Figure 4.1, decomposition temperatures of MWCNT were above 755 °C and more than 635 °C for COOH-MWCNT. A lower degradation temperature for the carboxylated MWCNT was expected as due to the decomposition of carboxylic acid functional groups attached to it. Based on the thermograms in Figure 4.1, decomposition temperatures of SWCNT were greater than 805 °C. COOH-SWCNT exhibited continuous decline in its mass with increments in temperature. SWCNT showed greater thermal stability than all MWCNTs. sSWCNT was shown to decompose at temperatures > 842 °C.

Based on this experiment, MWCNT, COOH-MWCNT, SWCNT and sSWCNT were demonstrated to have adequate thermal stability over the range of operating temperatures in which thermal desorption is typically performed. Due to the poor thermal stability of COOH-SWCNT over a wide range of temperatures, it was uncertain whether COOH-SWCNT could be utilized for TD applications. An additional TGA experiment was carried out during the optimization of the CNT sorbent thermal conditioning procedure to

determine if decomposition of the CNTs occurs during the cleaning process (Refer to Section 4.3.2.1).

4.3.1.2 Raman Spectroscopy

Raman spectroscopy was primarily used for evaluating the extent of disorderliness and defects in the CNTs. The existence of a double resonance D band at $\sim 1350\text{ cm}^{-1}$ denotes structural disorder associated to finite particle size, curvature defects on the graphene and defects induced by pentagons and heptagons (Stone–Wales defects) [20, 21]. Such disorder and crystallographic defects are commonly situated on the CNTs walls and ends [21, 22]. The appearance of a double resonance D' band at $\sim 1615\text{ cm}^{-1}$ is an indication of defects along the length of the CNTs [23]. The G band ($\sim 1582\text{ cm}^{-1}$) is attributed to intramolecular vibrations between carbon atoms and in-plane stretching of C-C bonds in

Figure 4.2: Raman spectra of (a) MWCNT and COOH-MWCNT (b) SWCNT (c) COOH SWCNT and sSWCNT measured by laser excitation at 633 nm.

Table 4.1: Summary of D, G and D' bands wavenumber and I_D/I_G ratio of MWCNT, COOH-MWCNT and SWCNT measured by Raman Spectroscopy.

Type of CNT	D band (cm^{-1})	G band (cm^{-1})	D' band (cm^{-1})	I_D/I_G ratio
MWCNT	1325	1574	1598	1
COOH-MWCNT	1328	1578	1602	0.9
SWCNT	1324	1584	-	0.02
COOH-SWCNT	1331	1587	-	0.18
sSWCNT	1328	1585	-	0.09

graphene [20, 24]. More order in the structure corresponds to lower D band and G band intensity ratios (I_D/I_G) [25]. The Raman spectra for all CNTs were depicted in Figure 4.2, while the spectroscopy data are summarized in Table 4.1. The presence of all three featured bands, D, G and D' bands were observed for both MWCNT and COOH-MWCNT. All SWCNTs only showed 2 distinctive bands, namely the D and G bands.

The presence of a D' band and higher I_D/I_G ratio in the two MWCNTs suggested that MWCNT and COOH-MWCNT are have more disorder and defects in their structures. This could be due to several graphene layers within MWCNTs and such defects are present along the walls of the tube structure or entangled within the internal surfaces.

4.3.2 Sorbent Tube Experiments

4.3.2.1 Removal and Desorption of Organic Impurities from Nanomaterials

Newly packed nano sorbent tubes had to be thermally conditioned for a prolonged period of time before the tubes could be first used. This is to eliminate any atmospheric organic species that were adsorbed onto the CNT surfaces or existing VOCs present during the CNT preparation process. A flow of inert gas (i.e. nitrogen) and high temperature heating were utilized to thermally desorb and remove the VOC impurities that could conceivably interfere with target VOC signals during the loading of standards or when sampling.

From the TGA results in Section 4.3.1.1, no considerable mass loss of CNT material was observed before 635 °C. The maximum operational conditioning temperature, 380 °C, was set on the TC-20 to maximize the desorption of VOCs retained on the nanomaterials. The sorbent tubes were subjected to different conditioning time periods and examined by TD-GCMS. The optimal amount of time necessary for the elimination of most organic contaminants was attained by adding all of the time taken to heat the tube at 380 °C to

obtain TIC chromatograms with negligible amounts of VOC present. As it was uncertain whether CNTs contained artifact peaks like conditioned conventional sorbent materials because there are no previous studies pertaining to this point, it was initially difficult to establish and define the mass of VOC leftover in the CNT sorbent that could be deemed as negligible. Therefore, the peaks of any remaining VOCs in the sorbents after heating for a known duration of time (to obtain the final "blank" chromatogram) were called artifacts and quantified by direct injection to determine the VOC amounts. The known amount of VOCs left in the nano sorbent material could be used to evaluate its significance when standards were injected into the CNT tubes.

Figure 4.3 reveals the progress of organic species removal and the blank chromatograms achieved after conditioning for the specified amount of time for the various CNTs. A number of VOCs were identified, such as xylenes, phenol, octanal, nonanal and decanal from the CNT chromatograms. This indicates that the CNTs are capable of adsorbing several VOCs at different surfaces during storage. Some compounds such as hexane are shown to have stronger adsorption on the CNT surfaces as much longer durations are required to desorb them. The reduction in these response signals with further conditioning implied that the sorbent tubes became cleaner.

Figure 4.3: TIC chromatograms of (a) MWCNT sorbent tube, (b) COOH-MWCNT sorbent tube, (c) SWCNT sorbent tube, (d) COOH-SWCNT and (e) sSWCNT sorbent tube after accumulated hours of conditioning. The chromatogram in red is the analysis of the sorbent tube at the optimized conditioning hours.

TGA was performed again for all CNT materials at 380 °C at the total amount of time required for achieving the final blanks for further experimentation. This was to ensure that there is no degradation in CNTs during thermal conditioning for the prolonged duration of time essential for removing organic contaminants. MWCNT, COOH-MWCNT and SWCNT were subjected to heat for 20 hours at 380 °C. The other SWCNTs were heated for 17 hours at 380 °C. The absence of degradation is demonstrated by insignificant change in CNT mass when the temperature was held constant at 380 °C for the time frames mentioned. Figure 4.4 illustrates the thermograms for all CNTs after

Figure 4.4: TGA thermograms for (a) MWCNT and COOH-MWCNT when isotherm at 380 °C for 20 hours, (b) COOH-SWCNT and sSWCNT when isotherm at 380 °C for 17 hours and SWCNT at the same temperature for 20 hours.

initial temperature increments to 150 °C to desorb water that was trapped on CNT surfaces. The thermograms showed that the mass losses are much higher for SWCNTs than MWCNTs during the first hour, suggesting that SWCNTs have higher moisture compared to MWCNTs. The percentage mass loss for MWCNTs and SWCNT is about 1% and 2% respectively after the first hour. About 5% loss in mass was noted for both sSWCNT and COOH-SWCNT when heated to 150 °C. There was no considerable loss in mass when a constant temperature of 380 °C was applied to all CNTs for subsequent hours of heating (i.e. 17 hours for sSWCNT and COOH-SWCNT; 20 hours for MWCNTs and SWCNT).

Hence, it can be concluded that during thermal conditioning of the sorbent materials for the stipulated durations (i.e. 13 hours for MWCNT, 16 hours for COOH-MWCNT, 20 hours for SWCNT, 12 hours for COOH-SWCNT and 9 hours for sSWCNT) will result in negligible decomposition in the CNTs.

Residual VOCs were still detected in all nano sorbents during TD-GCMS analysis of the final blank chromatograms despite long hours of conditioning. Identification of these interference compounds (i.e. artifacts) is important as high amounts represent a form of error during quantification. Figure 4.5 shows the final blank chromatograms of the various CNTs. The visible artifacts are labeled at their retention times (t_R).

Benzene (t_R : 16.15 min) and hexane (t_R : 14.17 min) were present in all CNTs. Toluene (t_R : 18.82 min) was identified in the blank SWCNT TIC chromatogram. The sources of artifacts could be from gaseous toluene and benzene, both carbon-containing chemicals that were provided into the catalytic CVD process to interact with the catalyst in order for the synthesis of CNTs to take place [26]. In addition, benzene is an intermediate in the CVD process [27]. It can be hypothesized that this intermediate compound undergoes

Figure 4.5: Artifacts identified and labeled in blank sorbent tube chromatograms of (a) MWCNT (b) COOH-MWCNT (c) SWCNT (d) COOH-SWCNT and (e) sSWCNT.

further reactions to form benzene derived compounds like toluene, under high temperature and carbonaceous conditions in the reaction vessel. These reagents and intermediates might have remained in the industrial-purified CNT materials and attempts to completely remove them via thermal conditioning of the sorbent tubes are not sufficient.

The artifacts found in the blanks were quantified by direct injection of VOC standards into the GCMS at concentrations between 0.02 ng and 10 ng to calculate the precise

Table 4.2: Mass of artifacts present in CNT after thermal conditioning for the specified (see text) amount of time required.

Type of CNT	Amounts of artifact present (ng)		
	Benzene	Toluene	Hexane
MWCNT	1.71	0	2.20
COOH-MWCNT	1.78	0	0.52
SWCNT	1.41	0.11	0.81
COOH-SWCNT	0.67	0	0.13
sSWCNT	1.07	0	0.17

amount of benzene, hexane and toluene in the CNT tubes (Table 4.2). The highest hexane mass (2.20 ng) was found in the MWCNT. It was also observed that both non-carboxylated CNTs have higher amounts of hexane compared to their carboxylated derivatives. This could be due to larger isosteric heat of adsorption for hexane on non-carboxylated (i.e. non-polar surfaces) CNTs, resulting in stronger adsorbate-adsorbent interactions [28, 29]. Functionalization of CNTs with carboxylic acid groups modified the polarity of the CNT surfaces, leading to easier desorption of hexane. While the amounts of artifacts contributed negligible errors to the injection of 500 ng VOC standards conducted in this study, these artifacts could interfere with the accurate determination of benzene and hexane at ultra-low levels. Therefore, these materials are probably not appropriate for trace analysis of those VOCs, although benzene and toluene artifacts are also commonly found in other commercially available sorbent materials such as Tenax and Carbopack X.

For the reuse of sorbent tubes, MWCNT tubes were thermally conditioned for 3 hours and SWCNT tubes were heated between 4.5 to 5.5 hours. The conditioning period for successive use of the sorbent tubes was determined after the TD-GCMS analysis of sorbents tubes spiked with 500 ng of the VOC mixture. The blanks after subsequent thermal conditioning were examined for interferences that could compromise the accuracy of the sampling method. Satisfactory blanks were achieved at the stipulated conditioning durations as the conditioned sorbent tube produced a blank chromatogram that overlaid well with its blank before the injection of VOC standards.

4.3.2.2 Thermal Desorption Properties of CNTs by Direct Loading of VOCs Solution

The desorption profiles of VOCs with various polarities and functional groups desorbed from all CNTs were investigated. 500 ng of 48 representative VOCs that are detected in the atmosphere in Singapore [4] were spiked into the 5 CNT tubes (MWCNT, COOH-MWCNT, SWCNT, COOH-SWCNT and sSWCNT) and a conventional multi-sorbent containing Tenax/Carbopack X. The multi-sorbent tube was utilized as a reference for desorption comparisons.

Figure 4.6 depicts the injection setup for the sorbent tube. Prior to injection, the flow rate of the nitrogen stream entering the tube was adjusted using the flow calibrator (Bios Defender 510) to 100 mL/min. 500 ng of the 48 VOC standards solution was loaded into the GC syringe and introduced into the sorbent tube via a calibration loading rig. The syringe was removed only after 20 seconds in the rig to achieve complete evaporation of VOCs from the syringe. The nitrogen gas flowed in the direction of injection to assist the movement and retention of the VOCs onto the sorbents' surfaces.

Figure 4.6: Assembly of sorbent tube during loading of VOC standards solution.

Loaded sorbent tubes were evaluated via TD-GCMS. The procedures were replicated for a total of 4 times (n=4), each time after cleaning the tubes using the subsequent conditioning methods mentioned in Section 4.3.2.1.

Repeated injections were used to observe if there were changes in the normalized peak area ratio of each VOC. The discrepancies in the ratios were used to determine the variation extent in the desorption efficiency of CNTs when the VOC loading cycles increased. From the chromatograms obtained, the peak area of each VOC quantifier ion was integrated and normalized against the analogous quantifier ion peak area under the same VOC from the Tenax/Carbopack X sorbent tube using the equation 4.1:

$$(\text{Peak area ratio})_{\text{VOC}} = \frac{(\text{VOC peak area})_{\text{CNT}}}{(\text{VOC peak area})_{\text{Tenax/carbopack X}}} \quad (4.1)$$

where $(\text{Peak area ratio})_{\text{VOC}}$ is the normalized peak area ratio of the VOC, $(\text{VOC peak area})_{\text{CNT}}$ denotes the VOC peak area from the CNT sorbent and $(\text{VOC peak area})_{\text{Tenax/carbopack X}}$ represents the VOC peak area from the conventional multi-sorbent tube. A normalized peak area ratio ≥ 1.1 represents significantly better desorption recovery of the VOC analyte from the CNT sorbent as compared to the conventional sorbent during thermal desorption. On the other hand, a peak ratio value < 0.7 suggests poorer recovery of the VOC from the CNT sorbent compared to the conventional sorbent material. A ratio between 0.7 and 1.1 denotes comparable desorption recovery of VOC analyte from CNT sorbent with minimal losses. The categorization of the recovery ratios were based on acceptable recovery ranges of analytes during method validation, which are typically between 70% to 110% [30-32]. The VOCs are classified based on their functional groups, together with their average peak ratios from four replicated measurements for each CNT (Table 4.3). The percentage relative standard deviations (%RSD) for the n=4 injections are also summarized in Table 4.3.

Table 4.3: The average and percentage relative standard deviation (%RSD) values of the normalized peak area ratios of VOCs for n=4. Compounds are classified according to their functional groups.

Type of Functional Group	Name of VOC	COOH-MWCNT		MWCNT		SWCNT		COOH-SWCNT		ssWCNT	
		Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD
Alcohol	isopropyl alcohol	0.10	20.32	0.15	22.46	0.49	14.98	0.23	13.76	0.25	12.03
Ether	ethyl ether	0.77	8.51	0.89	4.08	0.84	12.18	0.88	11.52	0.80	11.57
	isoprene	0.34	11.06	0.46	9.23	0.64	11.15	0.47	17.52	0.31	17.17
Alkene	1-octene	0.53	18.61	0.64	19.85	0.56	18.29	0.56	13.63	0.71	11.83
	2-methylpentane	0.95	1.92	0.95	13.51	0.84	13.97	0.89	10.71	0.75	16.30
	3-methylpentane	0.92	2.31	0.90	17.18	0.77	13.65	0.83	12.19	0.72	14.90
	hexane	0.78	9.01	0.81	10.81	0.73	10.11	0.74	10.13	0.79	9.11
	methylcyclopentane	0.88	8.58	0.96	2.55	0.79	9.58	0.84	1.24	0.82	8.93
	cyclohexane	0.79	8.51	0.92	1.07	0.75	11.29	0.81	5.52	0.77	9.99
Alkane	heptane	0.90	11.49	0.96	8.87	0.61	44.70	0.64	24.11	0.84	12.37
	methyl cyclohexane	0.89	6.50	0.94	14.68	0.80	7.15	0.82	8.55	0.85	9.12
	2-methylheptane	0.95	6.12	1.00	1.79	0.64	17.55	0.70	15.25	0.86	12.22
	octane	0.97	3.31	1.02	8.53	0.62	14.25	0.62	9.18	0.89	9.45
	nonane	0.94	7.72	0.99	1.33	0.39	31.53	0.52	12.90	0.76	10.34
	decane	0.93	5.10	0.98	4.03	0.37	19.38	0.66	11.82	0.79	8.15
Halogenated Alkanes	dichloromethane	0.39	9.05	0.31	59.38	0.85	12.37	0.70	14.22	0.82	8.26
	trichloromethane	0.50	16.32	0.69	11.51	0.61	19.13	0.26	31.63	0.56	13.20
Halogenated Alkenes	trichloroethylene	0.37	31.37	0.58	26.69	0.83	10.15	0.73	14.13	0.86	10.25
	tetrachloroethylene	0.49	22.26	0.60	27.43	0.77	9.72	0.64	12.90	0.79	10.48
	benzene	1.01	4.58	1.05	0.73	0.92	5.24	0.98	3.30	0.99	3.03
	toluene	1.01	0.72	1.11	10.54	0.94	4.12	1.00	1.44	1.01	1.65
	ethyl benzene	0.98	1.32	0.99	1.05	0.96	1.86	0.94	2.53	0.94	2.49
	<i>p,m</i> -xylene	0.98	2.56	1.00	1.55	0.95	2.75	0.95	2.29	0.96	9.36
	<i>o</i> -xylene	0.99	2.23	1.00	0.83	0.95	2.71	0.95	3.10	0.95	3.02
	2-ethyltoluene	0.98	1.39	1.00	1.39	0.95	2.66	0.94	1.84	0.94	2.75
Aromatic Compounds	3-ethyltoluene	0.97	2.32	0.98	2.50	1.02	4.16	0.98	0.74	0.97	2.29
	4-ethyltoluene	1.13	9.87	1.07	13.51	0.89	9.43	0.93	6.71	1.00	22.29
	1,3,5-trimethylbenzene	0.99	3.14	1.02	1.80	0.96	1.63	0.93	3.13	0.92	1.86
	1,2,4-trimethylbenzene	0.98	2.18	1.00	1.17	0.95	1.62	0.93	2.31	0.91	3.35
	1,2,3-trimethylbenzene	0.98	1.82	0.99	0.59	0.95	3.57	0.94	3.09	0.93	3.44

Table 4.3: The average and percentage relative standard deviation (%RSD) values of the normalized peak area ratios of VOCs for n=4. Compounds are classified according to their functional groups (continued).

Type of Functional Group	Name of VOC	COOH-MWCNT		MWCNT		SWCNT		COOH-SWCNT		sSWCNT	
		Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD	Average	%RSD
Carbonyl compounds	2-butanone	0.19	10.67	0.25	23.99	0.5	13.62	0.1	28.21	0.11	9.62
	methyl isobutyl ketone	0.28	20.18	0.36	36.54	0.71	13.19	0.23	33.7	0.14	22.36
	hexanal	0.22	5.74	0.22	6.46	0.41	16.42	0.2	17.91	0.18	13.46
	heptanal	0.14	12.88	0.16	22.1	0.34	16.34	0.25	11.82	0.14	10.28
	octanal	0.13	16.24	0.15	30.05	0.27	18.3	0.36	10.08	0.23	13.14
	nonanal	0.15	10.58	0.18	24.35	0.22	24.39	0.42	11.12	0.47	13.82
	decanal	0.18	20.3	0.19	19.9	0.16	39.78	0.37	14.27	0.64	14.51
	ethyl acetate	0.05	25.02	0.06	34.64	0.38	37.09	0.04	33.33	0.07	14.03
	methacrolein	0.27	17.38	0.37	16.41	0.77	10.5	0.58	15.77	0.59	12.85
	methyl methacrylate	0.15	24.6	0.16	14.18	0.52	13.47	0.13	23.29	0.13	36.67
Aromatic Ketones	acetophenone	0.46	16.89	0.52	17.03	0.7	11.5	0.58	6.94	0.37	10.92
Aromatic Aldehydes	benzaldehyde	0.82	12.2	0.87	9.62	0.94	9.56	0.61	6.45	0.64	7.18
Vinylbenzenes	styrene	0.92	2.55	0.96	1.08	0.88	5.42	0.89	2.78	0.83	8.16
Hydroxybenzenes	phenol	0.75	5.14	0.89	8.56	0.7	4.12	0.5	7.13	0.38	16.09
Heterocyclic	pyridine	0.79	4.91	0.91	5.13	0.83	9.96	0.85	7.99	0.78	13.38
Compounds	furfural	1	11.91	1.18	7.68	0.86	11.86	0.5	9.23	0.45	7.45
Cyanobenzenes	benzonitrile	0.98	2.18	1	0.92	0.97	2.68	0.94	1.44	0.95	3.21

The results revealed that each type of CNT has different adsorption characteristics for various functional groups. Both types of MWCNTs had 18 identical VOC analytes exhibiting normalized peak area ratios of < 0.7 , indicating poorer recovery in the CNT sorbent in comparison to the conventional sorbent. Out of these 18 VOCs, 16 of them contained polar functional groups: carbonyl compounds (i.e. esters, aldehydes, ketones), alcohols, halogenated hydrocarbons. The other 2 VOCs are non-polar alkenes: isoprene and 1-octene. 30 other VOCs of interest have peak ratios of ≥ 0.7 , implying similar recoveries to conventional Tenax/Carbopack X sorbents. This also indicates that the methanol solvent molecules have insignificant interference on their adsorptions. Most of them were non-polar except for 5 polar VOCs: pyridine, phenol, benzaldehyde, benzonitrile and furfural. Non-polar aliphatic compounds primarily adsorb by hydrophobic interactions on the surfaces of MWCNTs. The adsorption coefficients of non-polar aliphatic compounds are weaker than that of non-polar aromatics, which explains the slightly lower normalized peak ratios of alkanes when compared to aromatics for both MWCNTs [33].

Of the 30 VOCs with recovery ratios of ≥ 0.7 , it was observed that 17 aromatic compounds including heterocyclic aromatics pyridine and furfural have peak area ratios near to 1, or larger than 1.1 in the case of furfural. The high desorption recovery of aromatics from MWCNTs can be understood by adsorption/desorption hysteresis. Hysteresis is the phenomena when high adsorption capacity comes together with strong desorption of molecules [34]. The hysteresis adsorption mechanism is based on π - π interactions between aromatic molecules and the CNT surface. Upon adsorption, these π - π coupling interactions disrupts Van der Waals forces between CNTs and reduces aggregation of CNT bundles [35]. As a result, adsorption and desorption of aromatic molecules assume dissimilar pathways. Therefore, strong adsorption of aromatic VOCs

on the MWCNTs via π - π interactions is attained collectively with efficient desorption of these analytes.

SWCNTs, on the other hand, display affinity for other functional groups. 25 to 31 VOCs demonstrated comparable recoveries to the traditional multi-sorbent, suggesting that methanol does not affect their retention on the CNT sorbents. About 17 to 23 VOC analytes have poor desorption recoveries for all SWCNTs. Peak ratios < 0.7 were noted for VOCs with the following chemical functionalities: alcohols, alkenes, alkanes with 7 carbons and above, carbonyl compounds (esters, aldehydes and vinyl aldehydes). It is unlikely that the poorer ratios for the mentioned hydrocarbons are due to them being chemically affected by the solvent molecules as they are unreactive. Based on literature reports, alkanes were verified to adsorb and desorb from SWCNT at 3 unique sites: interior, groove and exterior. The amount of thermal energy needed to desorb alkanes at different sites are in ascending order: external $<$ groove $<$ internal sites [36]. Binding energies on SWCNT become larger when number of carbon atoms in the alkane main chain increases [37, 38] and alkane adsorption on the internal sites was reported to be kinetically favored [39]. This explains the poorer desorption of alkanes as the length of the carbon chain increases and becomes especially visible when there are 7 carbons and higher. Heptane, 2-methylheptane, octane, nonane and decane have peak area ratios < 0.7 . The energy provided during TD may not be adequate to overcome this strong binding energy within the interior adsorption sites, hence, absolute recovery of these alkanes were not attained.

The selectivity of SWCNT sorbents is observed to be weakly associated with polarity of VOCs based on the abnormally high recovery ratios obtained for polar analytes such as halogenated organic species and anomalously lower values for alkanes with at least 7

carbon atoms and above. It is probable that exemplary desorption recoveries of polar compounds like dichloromethane, tetrachloroethylene, trichloroethylene, methacrolein were due to displacements of those molecules to sites with lower adsorption energies; desorption was thus, more efficient. Earlier studies have shown that nonane molecules being more polarizable and possessing higher adsorption energy on SWCNT sites can displace carbon tetrachloride molecules that were originally adsorbed on internal sites to lower adsorption energies sites such as the groove or exterior sites[40].

In accordance to the EPA TO-17 requirements for repeatability, % RSD values were calculated to investigate the precision of multiple injections. The majority of the %RSD values for the normalized peak area ratios were < 25%, as established by EPA. The VOCs that had %RSD values >25% are dichloromethane, trichloroethylene, octanal and ethyl acetate in MWCNT, trichloroethylene and ethyl acetate in COOH-MWCNT, heptane, nonane, decanal and ethyl acetate in SWCNT, trichloromethane, 2-butanone, methyl isobutyl ketone, and ethyl acetate in COOH-SWCNT, and methyl methacrylate in sSWCNT. It was observed that these VOCs which fail to meet the EPA criteria are those with poor recoveries by thermal desorption (ie. low peak area ratios).

Alkenes, carbonyls and alcohols were the mutually common VOC groups that demonstrated low peak ratios for all types of CNTs. These functional groups are generally more reactive and have electron donor acceptor (EDA) properties, since there is electrophilicity and nucleophilicity in certain parts of their functionalities. While there is a possibility that their low recoveries are related to the methanol used to dissolve the target VOCs, other reasons such as irreversible binding at the adsorption sites or sorbent breakthrough are also plausible. To eliminate the other possible factors, the peak area ratios of these EDA VOCs from the first to the fourth injection were inspected for any

declining trend in all CNTs. No obvious decreasing variation is observed in the amount of VOCs desorbed during subsequent repeated injections. The %RSD values calculated in Table 4.3 illustrate that the adsorption and desorption capacity of the CNT sorbents are generally within 25% for most VOCs during each tube analysis. Compounds with %RSD above 25% show drastic changes in peak areas between injections, but not in continuous descending order. Thus there is no strong evidence to validate that the VOCs with low peak area ratios are attributed to continuous and irreversible adsorptions onto the sorbents, causing accumulation on the active sites of the CNT surfaces.

4.3.2.3 Effects of Surface Modifications and CNT Lengths on Desorption Recoveries

Welch's *t*-test for unequal variances was performed to investigate any significant differences in the analyte selectivity between the chemically modified and non-modified CNTs, as well as the CNTs with different lengths using equation 4.2.

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\frac{s_1^2}{N_1} + \frac{s_2^2}{N_2}}} \dots \dots \dots (4.2)$$

where *t* is the student *t*-test value, $\bar{x}_1$ and $\bar{x}_2$ are the mean VOC peak area ratios of two independent CNTs, *s*₁ and *s*₂ are the standard deviations of the VOC peak area ratios for *n*=4 for each CNT. *N*₁ and *N*₂ stand for the number of VOC peak area ratios for each CNT and the degree of freedom, *v*, is mathematically approximated as equation 4.3:

$$v \approx \frac{\left(\frac{s_1^2}{N_1} + \frac{s_2^2}{N_2} \right)}{\frac{s_1^4}{N_1^2 v_1} + \frac{s_2^4}{N_2^2 v_2}} \dots \dots \dots (4.3)$$

*s*₁ and *s*₂ are the standard deviations calculated for the two CNT data sets (i.e. peak ratios) that are used for comparison. *N*₁ and *N*₂ represent the number of VOC peak

Table 4.4: *t*-test values for their respective degree of freedoms v .

Name of VOC	MWCNT/COOH-MWCNT		SWCNT/COOH-SWCNT		sSWCNT/SWCNT	
	<i>t</i>	<i>v</i>	<i>t</i>	<i>v</i>	<i>t</i>	<i>v</i>
isopropyl alcohol	2.21	5	6.37	4	6.04	4
ethyl ether	3.26	5	0.51	6	0.67	6
isoprene	4.49	6	3.06	6	7.37	6
dichloromethane	0.86	3	2.09	6	0.49	5
2-methylpentane	0.05	3	0.72	6	1.06	6
methacrolein	2.66	6	2.96	6	3.13	6
3-methylpentane	0.35	3	0.9	6	0.65	6
hexane	0.53	6	0.25	6	1.13	6
2-butanone	1.85	4	10.71	4	11.42	3
trichloromethane	3.46	6	4.82	5	0.61	5
ethyl acetate	0.5	5	4.85	3	4.44	3
methylcyclopentane	1.84	4	1.24	3	0.49	6
cyclohexane	3.83	3	1.17	5	0.43	6
benzene	1.63	3	2.24	5	2.55	5
heptane	0.93	6	0.21	5	1.57	4
trichloroethylene	2.13	6	1.55	6	0.39	6
methyl methacrylate	0.35	5	10.36	4	9.01	5
methyl cyclohexane	0.68	4	0.59	6	1.08	6
methyl isobutyl ketone	1.1	4	7.82	6	11.59	4
pyridine	4.16	6	0.31	6	0.81	6
2-methylheptane	1.72	4	0.7	6	2.8	6
toluene	1.76	3	3	4	3.34	4
1-octene	1.39	6	0	6	2.3	6
octane	1.23	4	0.1	5	4.28	6
hexanal	0.04	6	5.43	5	6.53	4
tetrachloroethylene	1.15	5	2.25	6	0.37	6
furfural	2.4	6	6.44	4	7.69	4
ethyl benzene	1.81	6	0.95	6	0.86	6
<i>p,m</i> -xylene	1.08	5	0.01	6	0.09	4
nonane	1.2	3	1.77	5	4.98	5
heptanal	0.98	4	2.69	5	6.96	3
styrene	2.84	4	0.37	5	1.17	5
<i>o</i> -xylene	1.18	4	0.3	6	0.09	6
phenol	3.32	4	8.79	6	9.57	4
3-ethyltoluene	0.44	6	1.91	3	2.26	5
4-ethyltoluene	0.64	6	0.88	6	0.98	4
benzaldehyde	0.79	6	6.71	4	6.02	4
1,3,5-trimethylbenzene	1.77	5	1.54	5	3.31	6
decane	1.77	6	5.55	6	8.8	6
2-ethyltoluene	2.35	6	0.78	5	0.77	6
octanal	1.16	4	3.02	6	1.19	5
benzonitrile	1.96	4	1.91	5	1.03	6
1,2,4-trimethylbenzene	2.09	5	1.15	5	1.9	4
1,2,3-trimethylbenzene	1.16	4	0.24	6	0.94	6
acetophenone	1.06	6	2.66	4	7.26	4
nonanal	1.23	4	5.67	6	6.02	6
decanal	0.46	6	5.17	6	8.64	5

area ratios for each CNT. v_1 and v_2 are the individual degree of freedoms $N_1 - 1$ and $N_2 - 1$ respectively. The calculated *t*-test values between the VOC peak ratios of MWCNT and COOH-MWCNT in Table 4.4 revealed that 8 VOC desorption profiles showed significant differences at a confidence level at 95%. They are ethyl ether, methacrolein, isoprene, trichloromethane, cyclohexane, pyridine, phenol and styrene.

These compounds had lower recoveries from the COOH-MWCNT sorbent, as seen in Table 4.3. The result did not agree with a literature report [29] which proposed the improved desorption of polar analytes from COOH-MWCNT. This could be due to insufficient CNT surface modifications, as the wt% of COOH in COOH-MWCNT is very low.

For SWCNT and COOH-SWCNT, 18 VOC analytes demonstrated considerable differences at the 95% confidence levels as their *t*-test values are greater than their respective critical values. These target VOCs were: isopropyl alcohol, isoprene, methacrolein, 2-butanone, trichloromethane, ethyl acetate, methyl methacrylate, methyl isobutyl ketone, toluene, hexanal, furfural, phenol, benzaldehyde, decane, octanal, nonanal, decanal and heptanal. Most of the poorer desorption recovery ratios were from COOH-SWCNT (shown in Table 4.3) except for: toluene, decane, octanal, nonanal and decanal showing better peak area ratios in the functionalized SWCNT.

In conclusion, functionalization (with -COOH) can have an effect on the selectivity of EDA VOCs that were being retained and released during thermal desorption. 37.5% of the organic compounds exhibit evident differences in the peak ratios of SWCNTs, while 16.7% of the VOC species show distinct differences in the relative recoveries of MWCNTs, at a confidence level of 95%. While the effect seemed to be more prominent for SWCNTs than MWCNTs in this study, it cannot be concluded that SWCNTs are more susceptible to changes during surface modifications. This is because the mass packed, physical dimensions and %wt of functional groups are different for both types of CNTs. More studies are required to evaluate the extent of surface modification to the improvements of adsorption and desorption of VOCs.

The length of CNTs is also shown to have a major influence in the desorption recoveries of VOCs. 21 VOCs displayed significant differences at a confidence level of 95% when comparing the peak area ratios of sSWCNT and SWCNT. Out of the 21 VOCs, 14 organic species have better desorption recoveries in the longer SWCNT (refer to Table 4.3) and they are: isopropyl alcohol, isoprene, 1,3,5-trimethylbenzene, 2-butanone, methyl isobutyl ketone, hexanal, heptanal, ethyl acetate, methacrolein, methyl methacrylate, acetophenone, benzaldehyde, phenol and furfural. Longer CNTs have more available exterior binding sites than their shorter counterparts. As these sites have the lowest adsorption energies, better desorption of adsorbates were expected for longer SWCNTs. The 7 exceptions that exhibit higher peak area ratios in the shorter SWCNT are 2-methylheptane, octane, nonane, decane, toluene, nonanal and decanal. These compounds, other than toluene, were noted to have alkyl chains with 8 to 10 carbon atoms. Shorter length SWCNT have reduced interior sites for long-chain alkane adsorption due to the larger space occupied per molecule. More molecules of longer length aliphatic hydrocarbons were adsorbed onto binding sites that require lower amount of thermal energy to desorb them. Hence, higher peak area ratios were observed in the shorter SWCNT for these compounds. It is also possible that the ends of the CNTs are important for improved recoveries of these VOCs.

4.3.2.4 *Qualitative Breakthrough of VOCs in CNTs*

The purpose of the breakthrough experiments was to investigate one of the possible mechanisms causing poor recoveries in some VOC analytes such as aldehydes and alkenes from CNTs as mentioned in the Section 4.3.2.2. These target VOCs may be adsorbed very weakly on the CNT and consequently leak out of the sorbent material, resulting in considerable VOC losses. Improvisations were made to the traditional breakthrough setup for the CNT breakthrough experiments. Instead of attaching an exact

Figure 4.7: Sorbent tubes assembly for breakthrough experiment.

same CNT sorbent tube behind the first tube, a conventional Tenax/Carbopack X sorbent tube was attached to the back of the CNT sorbent tube using a Swagelok union as illustrated in Figure 4.7. The conventional multi-sorbent tube had been validated earlier in Chapter 2 Section 2.3.4 for its breakthrough during the injection of standards and all VOCs fulfilled the EPA breakthrough criteria ($< 5\%$). Minimal leakages present in the back conventional sorbent tube would indicate that the CNTs retained all VOCs strongly on/within their structures. Otherwise, weakly adsorbed molecules would bypass the CNT sorbent allowing the conventional sorbent tube at the back to absorb them.

High signals of these leaked VOCs would be reflected in the chromatogram obtained from the conventional sorbent tube. 1 μL of the 500 $\text{ng}/\mu\text{L}$ 48 VOC standards mix was loaded into the CNT tube using the calibration loading rig. Both sorbent tubes were analyzed by TD-GCMS. This experiment was performed on all types of CNT sorbent tubes and repeated for 4 times. Any analyte signal variations that were possible indications of breakthrough could be tracked when the experiment was repeated. Both MWCNTs detected dichloromethane (DCM) (t_{R} : 10.28 min) in the back conventional sorbent tubes, suggesting weak adsorption of DCM on these CNTs.

Figure 4.8: TIC chromatograms showing dichloromethane peak found in (a) MWCNT and (b) COOH-MWCNT corresponding to the conventional sorbent tube after breakthrough experiment.

The detection of DCM, however, was not replicated in all 4 breakthrough measurements. This suggests that DCM is not only weakly retained but inconsistently adsorbed in MWCNTs as well. Figure 4.8 shows the corresponding DCM signal for one particular injection for the conventional tube connected to both MWCNTs. Overall, MWCNT sorbent tubes still demonstrated exemplary adsorption capacity for the other 47 of the VOC analytes but are proven unreliable for analyzing DCM.

The back conventional tube attached to the SWCNT, COOH-SWCNT and sSWCNT sorbent tubes revealed no breakthrough leakages of the tested VOCs for all 4 breakthrough replicates. All SWCNTs displayed excellent adsorption capacity for all 48 VOCs. The higher surface areas present in SWCNTs relative to the MWCNTs could have offered larger adsorption surfaces for better retention of DCM upon loading [34]. Another postulation is that DCM and methanol compete for the same type of adsorption sites and the solvent molecules displaced DCM due to more stable binding. Polar molecules like DCM and methanol have more affinity for defective sites on CNTs [41].

The results of this breakthrough experiment confirmed that the poorer desorption efficiency of some EDA species such as carbonyl compounds could not be due to analyte breakthrough from the CNT sorbents. Breakthrough repeats that did not detect DCM

leakage in the back tube still displayed peak ratios values of < 0.7 for DCM, indicating low recovery. Nevertheless, all VOCs introduced into the front sorbent tube had not escaped from the CNT materials. This implies that the surface areas of the CNTs, together with the mass of packed CNTs were sufficient to adsorb all analytes, even in the possible presence of solvent molecules.

4.3.2.5 *Solvent Adsorption on CNTs*

The adsorption of methanol on CNTs is currently still debatable. It had been investigated in previous studies by computational, physical and analytical approaches. But there are few studies performed in this area for SWCNTs. We are not aware of studies regarding methanol adsorption on MWCNT. It was documented in one study using FTIR spectroscopy that SWCNT does not adsorb methanol when exposed to its vapors at room temperature for 10 minutes at 127 Torr [42]. On the other hand, another study obtained 89% methanol recovery on SWCNT relative to Tenax sorbent, implying strong adsorption of the compound on the CNT surface [18]. Computational calculations revealed that methanol is weakly adsorbed on a perfect SWCNT and on the armchair edge site, but strongly adsorbed on the zig zag edge sites of SWCNT with dissociation of the O-H bond [43].

The adsorption of methanol cannot be observed from the chromatograms, as the sorbent in the cold trap (i.e. Tenax) does not retain ultra-volatile compounds like methanol. While the most ideal scenario is that no methanol molecules were adsorbed during the loading of VOCs by solution injection, it is important to assume that some solvent molecules were also adsorbed onto the CNT surface. Physically, these molecules can compete with analyte molecules for binding at active sites of the CNTs. This could be the reason for

DCM breakthrough in MWCNTs since Raman Spectroscopy has shown that MWCNTs have more defects than SWCNTs. A computational simulation performed on SWCNT defects were shown in a previous study to have a positive role in promoting stronger adsorption of methanol [43]. The high flux of solvent molecules adsorbed on the CNT surfaces may also override the effect of chemical functionalization on the derivatized CNT surfaces, as observed on MWCNT and COOH-MWCNT having the same type of sorbent characteristics. The influence of methanol is much lesser for SWCNTs due to lesser defects present and a much higher %wt of COOH groups on COOH-SWCNT.

Chemically, methanol can undergo dehydrogenation in the presence of high temperatures (300 °C) and copper residuals in CNTs to yield formaldehyde [44-46]. Oxidation of methanol to formaldehyde can also occur when oxygen and oxides of iron, molybdenum and vanadium were present at temperatures between 250 to 400 °C [47]. Formaldehyde can undergo further reactions with alkenes such as the Prins reaction, aldol additions and aldol condensations [48, 49]. However, these reactions are only possible in aqueous media where hydronium ions can exist and not at high desorption temperatures (i.e. 380 °C). Hence, it is very unlikely that the solvent molecules chemically react with the EDA VOCs to form other products. No formaldehyde signals were observed in all CNT chromatograms due to the selectivity of the sorbent used in the cold trap.

4.3.2.6 *Suggestions to Low Alkene and Carbonyl Compound Recoveries*

Desorption recoveries and qualitative breakthrough investigations confirmed that poorer recoveries of VOCs such as alkenes and carbonyl compounds are not attributed to sorbent breakthrough or by accumulation on the active sites on CNT surfaces. Discussions in Section 4.3.2.5 explained that the chemical effects of solvent molecules with EDA analytes were quite unlikely.

ICPMS analysis was carried out to quantitatively evaluate the metallic impurities that the CNT materials contained. Metal nanoparticles are commonly employed during catalytic CVD synthesis of CNTs. Although these commercial CNTs have undergone post production purifications to remove the metal and amorphous carbon content, considerable levels of metal residues are still left in the CNT materials. Metal-catalyzed reactions that could potentially take place within the active sites of CNTs should be further explored as this could offer useful insights into the desorption profiles of VOCs obtained from these CNT materials. Table 4.5 summarizes the metal impurities detected in the CNTs. All types of CNTs contained dissimilar types of metallic residues with SWCNT having the widest range of residual metals present. All CNTs have high amounts of the main group elements (groups I, II and III) such as boron, sodium, magnesium, aluminium, potassium and calcium. Substantial quantities of nickel, molybdenum, iron, chromium, zinc, cobalt

Table 4.5: Major residual metal content in CNTs analyzed by ICPMS. <d.l. represents the concentration detected is below the detection limit of the ICPMS.

Elements	Concentration of elements (µg/g)				
	MWCNT	COOH-MWCNT	SWCNT	COOH-SWCNT	sSWCNT
Sc	22.6	<d.l.	4.08	0.21	<d.l.
Ti	384	4.07	17.4	6.98	2.44
V	0.23	0.15	5.53	7.14	0.50
Cr	16.5	13.6	829	730	46.3
Mn	2.35	1.65	19.2	40.4	5.28
Fe	73.1	66.4	876	1640	37.1
Ni	2550	7060	54.8	92.1	26
Co	3.22	7.87	472	528	1105
Cu	2.6	<d.l.	25.5	19.8	1.08
Zn	196	355	83.7	52.1	98.7
Y	2.15	0.09	0.16	0.45	0.03
Zr	0.77	0.27	4.08	37.1	0.06
Mo	1.57	0.86	1280	247	48.0
Ru	0.02	0	0.01	0.01	0
Rh	0.04	0.01	0.01	0	0
Pd	0.88	0.09	0.11	0.41	<d.l.
Ag	<d.l.	0.79	0.99	0.10	<d.l.
Cd	0.19	0.03	0.39	0.31	0.75
La	105	22.2	11.9	18.8	0.85
Hf	0.51	0.07	0.42	0.60	0
Ta	0.31	0.22	0.31	0.03	0.03
W	0.42	0.17	0.26	0.15	<d.l.
Re	0	0	0.02	0.01	<d.l.
Os	0.04	0.02	0.01	0.20	0.14
Ir	0.07	0.04	0.03	<d.l.	0.02
Pt	2.29	3.13	0.51	8.31	3.62
Au	5.48	0.09	0.09	0.23	0.02

Table 4.5: Major residual metal content in CNTs analyzed by ICPMS. <d.l. represents the concentration detected is below the detection limit of the ICPMS (continued).

Elements	Concentration of elements (µg/g)				
	MWCNT	COOH-MWCNT	SWCNT	COOH-SWCNT	sSWCNT
Hg	1.01	0.29	0.21	0.15	0.09
Li	<d.l.	<d.l.	0.15	0.65	0.44
Be	0.03	<d.l.	<d.l.	0	0
B	6.11	13.7	50	125	43.2
Na	295	111	204	73.6	270
Mg	77.9	62.5	430	392	183
Al	38.6	27.9	297	67.0	21.8
K	132	11.2	24	53.5	237
Ca	185000	1820	6220	2040	1118
Ga	4.00	1.41	2.77	1.00	0.29
Ge	0.02	0	0.10	0.11	0.01
As	1.91	1.95	3.4	0.78	0.25
Se	0.83	<d.l.	<d.l.	0.09	<d.l.
Rb	0.24	0.06	0.09	0.07	0.25
Sr	34.8	3.25	16.4	7.21	4.92
In	0.03	<d.l.	0.01	<d.l.	<d.l.
Sn	0.6	0.15	1.75	0.31	<d.l.
Sb	8.84	0.15	0.32	0.05	0.03
Te	0.16	0.06	0.03	0.01	<d.l.
Cs	0.01	0.01	0.03	0.01	0.09
Ba	27.9	9.42	19.1	5.37	1.62
Ce	1.73	0.28	24.7	10.3	<d.l.
Pr	0.01	0	0.03	0.02	0
Nd	0.03	0.01	2.70	1.48	0
Sm	0.01	0	0.02	0.01	0
Eu	0.01	0	0.01	0.01	0
Gd	0.01	0	0.06	0.14	<d.l.
Tb	0	0	0.01	0.01	<d.l.
Dy	0	0	0.02	0.03	0
Ho	0	0	0	0.01	0
Er	0	0	0.14	0.08	0
Tm	0.04	0	0	0.01	0
Yb	2.42	0.08	0.04	0.05	0.01
Lu	0	0	0	0.01	0

and lanthanum were also found in all of the CNTs. Majority of these metals are primarily employed in the catalytic synthesis of CNTs. Other residual metals of lower levels could originate from chemical and physical manipulations during the generation of CNTs [50]. It was mentioned earlier in the literature that these metallic impurities cannot be completely eliminated despite thorough “washings” using nitric acid and they can also contribute as catalysts in electrochemical reactions [51]. Hence, it is rational to suggest that these residual transition metals are catalytically active and can participate in reactions with the target organic species, especially considering that the desorption step occurs at high temperatures. This could offer a reasonable explanation for the poor recoveries of certain VOCs as evident from the peak area ratios in Table 4.3.

Desorption recoveries and qualitative breakthrough investigations verified that lower recoveries of VOCs such as alkenes and carbonyl compounds are not the result of leakages due to sorbent breakthrough or permanent bindings on the active adsorption sites of CNT surfaces. Those compounds are observed to have reactive functionalities that are electrophilic or nucleophilic at different atoms. They could have reacted with one another, in the presence of the residual metals behaving as catalysts, to generate other higher boiling organic compounds which are undetected during the stipulated duration of time for the GC oven temperature program. At higher temperatures together with transition metals in proximity, the following metal-catalyzed reactions can potentially take place:

- 1) Oxidation of alcohols to aldehydes in the presence of oxygen and oxides of iron, molybdenum and vanadium at temperatures between 250 to 400 °C [47].
- 2) Molybdenum catalyzed olefin metathesis [52].
- 3) Molybdenum oxide catalyzed alcohol reactions [53].
- 4) Dehydration of isopropyl alcohol using iron-oxide catalyst [54].
- 5) Meerwein–Ponndorf–Verley reduction and Oppenauer Oxidation between carbonyl compound and alcohol [55, 56].

In general, the existence of metal residues may enhance the chemical reactivity of the analytes adsorbed on the sorbent material, resulting in side reactions. The list above contains reactions that the particular transition metals are known to catalyze. However, the likelihood of such reactions in CNTs remains inconclusive and will be the subject of future studies.

4.3.2.7 *Exposure of CNTs to Laboratory Air*

CNTs have been used for several applications such as electrode catalyzed reactions, catalytic dehydrogenation of *n*-butane, and growing of nanocrystals within CNT tube channels [57-59]. However, during the course of investigating the CNTs' potential as sorbents for trapping ambient organic pollutants, it has led to concerns of their storage and transportation during various types of experiments since they are likely to spontaneously absorb many VOCs naturally present in the atmosphere.

Adsorbed organic species might become involved in chemical reactions, generating unwanted side products, affecting reaction rates or acquiring false positives or inaccurate data for CNTs. SEM and TEM imaging of CNTs will not detect organic molecules due to their size and existing CNT purification procedures are mainly to minimize the presence of inorganic and metal residuals. Hence, it is important to identify the trapped organic impurities and amount of interferences on CNTs after being subjected to exposure for known duration of time in a laboratory environment.

A preliminary experiment was conducted using MWCNT, COOH-MWCNT, SWCNT, COOH-SWCNT and sSWCNT sorbent tubes. They were placed uncapped on the bench in an analytical laboratory and left exposed in air for 72 hours. TD-GCMS analysis was performed for all CNT sorbent tubes to qualitatively identify the VOCs that were adsorbed. All sorbent tube chromatograms after 72 hours of ambient air exposure are shown in Figure 4.9. Mass spectrums of 48 VOC s standards were used to determine the relative abundance of qualifier and quantifier ions with respect to the base ion for each compound. Qualitative identification was performed by matching the relative abundance of qualifier ions and t_{RS} of unknowns to the standards.

Table 4.6 summarizes the presence or absence of VOCs that were adsorbed onto the

Figure 4.9: TIC chromatograms of (a) MWCNT, (b) COOH-MWCNT, (c) SWCNT, (d) COOH-SWCNT and (e) sSWCNT after 72 hours of exposure in ambient air.

Table 4.6: The identity and relative abundance of qualifier ions, the retention times (t_R) of VOC analytes and the absence (x) and presence (✓) of different CNT sorbents.

Target Analytes	Qualifier ions		t _R (min)	VOCs detected in CNT sorbents				
	Q1	Q2		MWCNT	COOH-MWCNT	SWCNT	COOH-SWCNT	sSWCNT
isopropyl alcohol	43 (17)	59 (5)	8.21	X	X	✓	X	X
ethyl ether	45 (65)	73 (12)	8.80	✓	✓	✓	✓	✓
isoprene	68 (69)	53 (54)	9.11	✓	✓	✓	✓	✓
dichloromethane	49 (90)	86 (65)	10.27	✓	✓	✓	✓	✓
2-methylpentane	43 (100)	42 (53)	13.01	✓	✓	✓	✓	✓
methacrolein	41 (84)	39 (73)	13.25	✓	✓	✓	✓	✓
3-methylpentane	56 (87)	41 (52)	13.63	✓	✓	✓	✓	✓
hexane	41 (60)	43 (51)	14.21	✓	✓	✓	✓	✓
2-butanone	43 (100)	57 (8)	14.26	X	X	✓	X	✓
trichloromethane	85 (67)	47 (17)	14.70	✓	✓	✓	✓	✓
ethyl acetate	61 (19)	70 (15)	14.79	X	X	✓	✓	✓
methylcyclopentane	69 (48)	41 (42)	15.05	✓	✓	✓	✓	✓
cyclohexane	56 (95)	41 (43)	15.98	✓	✓	✓	✓	✓
benzene	77 (22)	51 (12)	16.16	✓	✓	✓	✓	✓
heptane	43 (100)	57 (64)	16.89	✓	✓	✓	✓	✓
trichloroethylene	132 (97)	134 (31)	16.97	✓	✓	✓	✓	✓
methyl methacrylate	41 (85)	39 (46)	17.27	X	X	X	X	X
methyl cyclohexane	55 (61)	98 (46)	17.58	✓	✓	✓	X	✓
methyl isobutyl ketone	58 (48)	85 (25)	17.95	X	X	X	X	X
pyridine	52 (47)	51 (21)	18.10	X	X	X	X	X
2-methylheptane	43 (78)	70 (26)	18.37	✓	✓	✓	✓	✓
toluene	92(64)	65(10)	18.70	✓	✓	✓	✓	✓
1-octene	41 (77)	70 (90)	18.88	X	X	X	✓	✓
octane	85(71)	57 (49)	19.04	✓	✓	✓	✓	✓
hexanal	57 (71)	72 (33)	19.14	✓	✓	✓	✓	✓
tetrachloroethylene	164 (77)	129 (65)	19.58	✓	✓	✓	✓	✓
furfural	95 (91)	39 (33)	19.95	X	X	✓	✓	✓
ethylbenzene	106 (38)	77 (8)	20.63	✓	✓	✓	✓	✓
m,p-xylene	106 (56)	77 (12)	20.86	✓	✓	✓	✓	✓
nonane	43 (91)	85 (48)	21.00	X	X	✓	✓	✓
heptanal	55 (66)	57 (55)	21.16	X	X	✓	✓	✓

Table 4.6: The identity and relative abundance of qualifier ions, the retention times (t_R) of VOC analytes and the absence (x) and presence (✓) of different CNT sorbents (continued).

Target Analytes	Qualifier Ions		t _R (min)	VOCs detected in CNT sorbents				
	Q1	Q2		MWCNT	COOH-MWCNT	SWCNT	COOH-SWCNT	sSWCNT
styrene	103 (46)	78 (37)	21.29	✓	✓	✓	✓	✓
<i>o</i> -xylene	106 (54)	105 (21)	21.39	✓	✓	✓	✓	✓
phenol	66 (24)	65 (20)	22.38	✓	✓	✓	✓	✓
3-ethyltoluene	120 (42)	91 (14)	22.60	✓	✓	✓	✓	✓
4-ethyltoluene	120 (39)	91 (12)	22.68	✓	✓	✓	✓	✓
benzaldehyde	106 (97)	77 (87)	22.74	X	X	✓	✓	✓
1,3,5-trimethylbenzene	120 (62)	91 (11)	22.85	✓	✓	✓	✓	✓
decane	43 (74)	71 (45)	22.90	✓	✓	✓	✓	✓
2-ethyltoluene	120 (42)	91 (13)	23.05	✓	✓	✓	✓	✓
octanal	43 (94)	57 (94)	23.13	X	X	X	✓	X
benzonitrile	76 (32)	50 (10)	23.18	✓	✓	✓	✓	✓
1,2,4-trimethylbenzene	120 (59)	91 (11)	23.41	✓	✓	✓	✓	✓
1,2,3-trimethylbenzene	120 (51)	91 (10)	24.03	✓	✓	✓	✓	✓
acetophenone	77 (66)	120 (27)	24.82	✓	✓	✓	X	✓
nonanal	41 (70)	70 (40)	25.03	X	X	X	X	X
decanal	41 (81)	70 (58)	27.03	X	X	X	X	X

different CNTs, their t_{RS} and relative abundances ratio of various ions with respect to the base ion. Several VOCs in the laboratory air were adsorbed on the CNT materials during the 72 hours of exposure. A total of 33 VOCs were detected in MWCNTs and between 37 to 40 compounds detected in SWCNTs. The most visible signals present in all chromatograms belonged to 2-methylpentane, 3-methylpentane, hexane, benzene and toluene. VOCs that were adsorbed on some but not all CNTs were generally alkenes, carbonyl compounds and alcohols except for methyl cyclohexane and nonane.

The preliminary data showed that organic compounds retained on the CNTs during exposure to air could potentially participate in chemical reactions. Previously in Section 4.3.2.1, the optimization of CNT conditioning procedures revealed that multiple VOCs were adsorbed during prolonged storage and required numerous hours of thermal conditioning to desorb from the CNT material. With the garnering interest in utilizing CNTs as a reaction vessel or as a catalyst-support in chemical reactions, it is important to look into methods of proper containment and purification to simultaneously reduce inorganic and organic contaminants prior to its actual application [60, 61].

4.3.2.8 *Active Sampling of Atmospheric VOCs using SWCNT*

Air samples were obtained by active sampling using the SWCNT tube as it gives the best desorption profiles for the tested VOCs among all nano-sorbents. A conventional Tenax/Carbopack X sorbent tube was used for comparison. Each sorbent tube was connected to a calibrated air pump (SKC pocket pump 210-1002, USA) and placed on the rooftop of the SPMS. The air flow was calibrated to 20 mL/min. 2.4 L of air was acquired after 2 hours and the sorbent tubes analyzed using TD-GCMS. Peak area ratios for each VOC detected was calculated using equation 4.1 and summarized in Table 4.7. The offset TIC chromatograms of the 2 sorbent tubes after sampling are shown in Figure

Table 4.7: Normalized peak area ratio of target analytes detected in SWCNT sorbent tube after collecting 2.4 L of air sample at the roof of SPMS building. 0 represents not detected in the SWCNT while N.A. represents the absence in both SWCNT and Tenax/Carbopack X.

Type of Functional Group	Name of VOC	Normalized peak area ratio
Alcohol	isopropyl alcohol	0
Ether	ethyl ether	N.A.
Alkene	isoprene	0
	1-octene	N.A.
Alkane	2-methylpentane	1.22
	3-methylpentane	1.11
	hexane	1.32
	methylcyclopentane	0.96
	cyclohexane	1.08
	heptane	0.66
	methyl cyclohexane	1.07
	2-methylheptane	N.A.
	octane	0.36
	nonane	0.22
Halogenated alkanes	decane	N.A.
	dichloromethane	1.53
Halogenated Alkenes	trichloromethane	N.A.
	trichloroethylene	1.18
Carbonyl Compounds	tetrachloroethylene	1.13
	2-butanone	0.2
	methyl isobutyl ketone	0
	hexanal	0
	heptanal	N.A.
	octanal	0
	nonanal	0
	decanal	0.33
Aromatic Compounds	ethyl acetate	0.22
	benzene	0
	toluene	1.1
	ethyl benzene	0.96
	<i>p,m</i> -xylene	0.96
	<i>o</i> -xylene	0.92
	2-ethyltoluene	0.83
	3-ethyltoluene	0.8
	4-ethyltoluene	0.77
	1,3,5-trimethylbenzene	1.07
Vinyl Carbonyls	1,2,4-trimethylbenzene	0.64
	1,2,3-trimethylbenzene	0.73
Aromatic Ketones	methacrolein	3.17
	methyl methacrylate	N.A.
Aromatic Aldehydes	acetophenone	0
	benzaldehyde	1.1
Vinylbenzenes	styrene	2.98
Hydroxybenzenes	phenol	1.36
Heterocyclic Compounds	pyridine	N.A.
	furfural	N.A.
Cyanobenzenes	benzonitrile	N.A.

Figure 4.10: Sample chromatograms of the (a) conventional Tenax/Carbopack X multi-sorbent tube, and (b) SWCNT sorbent tube after collecting 2.4 L of air.

Figure 4.11: Quantifier ion peak area of selected VOC signals in SWCNT and Tenax/Carbopack X, relative to each other in samples. VOC analytes were classified according to their functional groups: (a) Comparisons between saturated hydrocarbons, (b) Comparisons between aromatic hydrocarbons, (c) Comparisons between carbonyl compounds and (d) Comparisons between saturated and unsaturated halides.

4.10. 10 VOCs were absent in both sorbent tubes during sampling. 38 VOC target analytes were identified in the multi-sorbent Tenax/Carbopack X tube sample whereas 30 VOC analytes were present in the SWCNT sample tube. Out of the 30 analytes identified in the SWCNT tube, 7 VOCs have peak area ratios < 0.7 . They are 2-butanone, decanal, ethyl acetate, heptane, octane, nonane and 1,2,4-trimethylbenzene. Figure 4.11 shows the quantifier ion peak area of selected target compounds in both sorbent tubes classified according to their functional groups.

Compounds that were found in the Tenax/Carbopack X multi-sorbent tube but not in the SWCNT sorbent tube are isopropyl alcohol, isoprene, benzene, methyl isobutyl ketone, hexanal, octanal, nonanal and acetophenone. The results from sampling are in agreement with the functional group trends observed in Section 4.3.2.2 during the loading of the VOC standards onto the CNT materials, except for benzene and 1,2,4-trimethylbenzene. The discrepancies between the benzene ratios in sample tubes and in VOC standards tubes were deemed to be an artifact interference error. The compound is inherently generated from both sorbent materials during heating and the amount of benzene from sampling is very low. After background benzene subtraction, zero was seemingly obtained on the CNT tube while very low signal intensity was acquired from the Tenax/Carbopack X tube. Additional investigations are necessary to evaluate the artifact formation problem. The percentage error contribution of the artifact peak that could lead to inaccuracies of the values calculated, had to be verified. The determination of the maximum permissible error that does not considerably change the peak area ratio is valuable to the accuracy of the ratios calculated. In addition, the influences of humidity and temperature on CNT breakthrough during air sampling have to be further evaluated. Although there is no breakthrough of 1,2,4-trimethylbenzene in the SWCNT during the loading of standards, it may occur during sampling when humidity and temperature in the

atmosphere are sufficiently high. Humidity and temperature are two important factors that could possibly be the explanation for lower peak area ratio of 1,2,4-trimethylbenzene during sampling. As this study is a preliminary investigation on the potential analytical application of CNTs, detailed findings will have to be thoroughly discussed in the future.

Notably better recoveries were observed for $\frac{1}{3}$ of the VOCs detected in SWCNT when the peak areas were compared to the conventional sorbent during sampling. Methacrolein has the highest ratio and the signal response is about 3.2 times higher than conventional multi-sorbent tube. Styrene is next and has a peak area 2.98 times higher than the conventional sorbent material. DCM has a peak abundance that is 1.53 times higher when using the SWCNT sorbent tube for active sampling. Other compounds having peak area ratios > 1.1 include phenol, hexane and 2-methylpentane.

More thorough sampling experiments such as varying the air sample volume and flow rates, as well as the determination of the breakthrough in CNT tubes during ambient air sampling have to be performed to attain a better understanding of the behavior of the SWCNT sorbent. The findings of this experiment could serve as preliminary data for development of sampling methods using SWCNT sorbents.

4.4 Conclusion

The potential of CNTs as feasible TD sorbents for 48 VOCs with various functionalities was assessed by a calibration loading rig injection method coupled with TD-GCMS analysis. Instead of loading gas phase standards, the VOC standards solution was directly injected into the sorbent tubes and analyzed. Methanol was chosen since it does not retain on conventional sorbent surfaces but was suggested to have strong adsorption and desorption on CNTs by other publications [16]. The effects of methanol on the adsorption of 48 VOCs on CNTs were discussed and the feasibility of the injection method for TD-

GCMS analysis of CNTs was evaluated. TGA shows that all CNTs degraded at temperatures beyond the working range of the TD-GCMS, ensuring thermal stability during analysis. It also confirmed that there is no degradation in all CNTs when heated at 380°C, ensuring thermal stability during TD-GCMS analysis and thermal conditioning. Raman spectroscopy performed on the CNTs offered evidence for the existence of defects which acted as high energy adsorption sites for analytes. MWCNTs were observed to have more defects than SWCNTs, which could be the reason for DCM breakthrough on MWCNTs due to competition for defective sites and stronger binding to methanol molecules. ICPMS analysis detected numerous metallic impurities, primarily nickel, molybdenum, iron, cobalt and calcium. Transition metal residues could potentially be involved in catalytic reactions of VOCs when in direct contact at elevated temperatures. Initial conditioning times for the MWCNT and COOH-MWCNT tubes were optimized to be 13 hours and 16 hours, respectively. As for SWCNT, sSWCNT and COOH-SWCNT tubes, initial conditioning periods were optimized to be 20 hours, 12 hours and 9 hours, respectively. Subsequent conditioning methods were programmed at 3 hours for MWCNTs and between 4.5 to 5.5 hours for SWCNTs. All CNTs contained hexane and benzene artifacts. SWCNT had an additional toluene artifact detected.

Desorption experiments that were carried out by spiking 500 ng of 48 VOC standards into the 5 CNT sorbent tubes and analyzed using TD-GCMS have revealed that the injection method can be utilized for loading compounds with comparable peak area ratios in the CNTs. In MWCNTs, high desorption recoveries of non-polar and aromatic VOCs were achieved, especially towards aromatic compounds. Exemplary desorption recoveries of aromatic VOC compounds was explained by the hydrophobic interactions and π - π coupling between CNT and VOCs which were overcome easily by thermal desorption. The results also suggested that the adsorptions of aromatics and non-polar VOCs are not

significantly affected by solvent molecules from the VOC solution. Unexpectedly, there were no distinct differences between the desorption characteristics of the carboxylated and non-carboxylated MWCNT. A low wt% of -COOH groups on the derivatized CNTs might not be sufficient for any major changes in the desorption abilities of the material.

SWCNT, on the other hand, demonstrated strong desorption recoveries for 25-31 VOCs including aromatic compounds, halogenated hydrocarbons, pyridine and furfural. The solution injection method is shown to be feasible for them. The major similarity between SWCNTs and MWCNTs is the exemplary recoveries for aromatic VOCs, while the most prominent difference between them is the weak recoveries of alkanes beyond 7 carbons. The low peak ratios of these alkanes in SWCNT were due to larger binding energies on SWCNT with increasing number of carbon atoms in the alkane main chain.

Breakthrough evaluation performed on the SWCNTs demonstrated that they display strong adsorption capacity for all 48 VOC analytes. Irregular appearances of DCM signals during the 4 replicates of the breakthrough experiment was observed for all MWCNTs. DCM leakage variations signify weak and inconsistent adsorption of the compound by the MWCNTs and probably indicate that DCM and methanol competes for the same type of adsorption sites and the solvent molecules have displaced DCM due to more stable binding. Polar molecules like DCM and methanol have more affinity for defective sites on CNTs [41].

In the final section, analysis of CNT sorbents exposed to a chemistry laboratory environment for 72 hours unveiled a large number of VOCs retained on the CNTs during exposure. As there are chances that these trapped contaminants may participate in reactions or vary reaction yields, it is crucial to review the appropriate methods for eliminating organic impurities in CNTs prior to their applications. The sampling of

outdoor air using SWCNT and conventional sorbent tubes coincides well with the desorption profiles obtained from injection of VOC standards into the SWCNT tube.

Overall, SWCNT demonstrated the best potential as a sorbent material for VOC analysis based on the preliminary data acquired in this report. The following desirable properties of SWCNT were observed: high thermal stability, high adsorption capacity, sufficient desorption efficiency for VOCs of interest attributed to lesser sites of defects.

More experiments are essential to verify whether the existence of transition metal residues in CNTs will result in catalytic reactions between VOCs. This could be determined by synthesizing CNT-metal composites with known amount of metal incorporated and utilizing them as sorbents. Another approach is to use the CNTs as sorbents after additional purification steps to reduce inorganic impurities. Additionally, the effects of humidity, temperature and sampling breakthrough tests on CNTs have to be established to reduce the errors arising from the peak area ratio calculations before analytical procedures can be developed and validated.

4.5 References

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Conclusion

The analysis of the constituents in air pollution is one of the most fundamental aspects of safeguarding human health and the natural environment. It is also arguably the most important, as it provides quantitative information required for formulating solutions and establishing regulatory measures to control the problem. TD-GCMS is valuable for measuring various types of organic pollutants such as parabens, chemical warfare agents, PAHs and semi-volatile pesticides that are found in the natural environment and those emitted from micro-environments such as manufacturing industries and municipal waste plants. Environmental applications of TD-GCMS for VOCs has been explored and discussed in this report using an active sampling approach. All the findings reported in this work have provided extensive information on (i) an analytical procedure established for the determination of target organic pollutants, (ii) the compositions of atmospheric VOCs found in the western industrialized region of Singapore which was previously not reported by the NEA, and (iii) the incorporation of CNTs as potential TD sorbents for analyzing those VOCs.

An analytical method was developed and described in Chapter 2 for the quantification of 48 atmospheric volatile organic species that were identified in Western Singapore by active sampling using Tenax/Carbopack X multi-sorbent tubes. The separation of VOCs by the GC column was improved and the final temperature GC oven program was set at 30 °C for 12 min, raised to 60 °C at 30 °C/min, followed by another elevation to 124 °C at

40 °C/min. The temperature was kept at 124 °C for 2 min before increasing at 9 °C /min to the final temperature of 200 °C, which was maintained for 3 min before the termination of the run. The TD parameters were optimized after the modification of the VOC separation to facilitate better recovery of VOCs during each intermediate stage during the process. Throughout desorption of the sorbent tube, the temperature was kept at 280 °C for a duration of 10 minutes and the desorb flow was programmed at 45 mL/min without any split flow. The hydrophobic Tenax Peltier trap was cooled at -10 °C during primary desorption. During desorption of the trap, the temperature was maintained at 300 °C for 7 minutes using a split flow of 6 mL/min.

Various analytical method characteristics were validated using commercially available VOC standards. The GC separation of the target compounds was found to be highly specific using 100 ng of the VOC standards. 35 compounds had resolutions above 1.5, 10 were moderately separated with resolutions between 0.745 and 1.33 and there is a coelution of 2 isomers (*p*-xylene and *m*-xylene). The precision of all 46 VOC targets at 100 ng falls between 1 to 7% relative standard deviation (%RSD). Coefficients of determination (R^2) obtained for concentrations between 0.02 ng to 500 ng, ranged from 0.9909 to 0.9999. Breakthrough values of 500 ng VOC standards in a sorbent tube were between 0 to 2.13%. Tube desorption efficiencies of 200 ng analyte mixture were 92.1% to 100% while accuracy values were between 61% to 120% for 500 ng VOCs. LOD of target analytes were between 0.01 ng and 1.31 ng while LOQ values were between 0.02 ng and 2.24 ng.

The performance of the sorbent tubes was evaluated using different sampling volumes and flow rates. 30 mL/min was chosen as the optimum flow rate for sampling. Sampling volumes of 1 L and 5 L both demonstrated the best sorbent performance in reproducibility and breakthrough. Most of the target analytes established satisfactory breakthrough $\leq 5\%$,

reproducibility $\leq 20\%$ deviation and method detection limits < 0.5 ppbv. The requirements of the EPA for sorbent tube active sampling (i.e. EPA TO-17) were met for most target VOCs. Dichloromethane failed the breakthrough criteria at all sampling volumes and flow rates whereas pyridine was not detected during sampling experiments. Therefore, the method was found to be valid for 46 VOCs of interest.

The quantitative assessment method developed for the 46 VOCs was used for monitoring the ambient air in a western industrialized region of Singapore over a one year period from 1st February 2012 to 31st January 2013 and the results are discussed in Chapter 3. 517 samples were collected and analyzed using several approaches, such as simple statistics, computational modeling and health risk analysis. More than half of the intra-day concentration patterns for hydrocarbons were linked to man-made sources such as automobile exhausts and industrial processes. 44% of the carbonyl species daily trends registered maximas in samples collected between mornings to early afternoons, where the average temperature and sunlight intensity were at their peak. The annual VOC statistics show that toluene, 2-methylpentane, hexane, ethyl acetate and styrene are highly abundant in ambient air. The toluene concentration had the highest maximum of all the measured VOCs at $100 \mu\text{g m}^{-3}$, which is similar to concentrations detected in Kolkata, India [1]. The overall mean toluene concentration is similar to observations in Munich, Tokyo, London and Lille but only 12% of the average in major cities in the Philippines and Thailand [2-6].

Monthly box and whisker analysis unveiled that 8 VOCs (i.e. 2-butanone, 4-ethyltoluene, benzene, cyclohexane, methyl methacrylate, decanal, isopropyl alcohol and 3-methylpentane) had the highest monthly mean values in September 2012 and 36 VOCs exhibited increments in average monthly concentrations between August to October 2012. 6 VOCs (i.e. 2-butanone, cyclohexane, 2-ethyltoluene, furfural, methyl methacrylate and

trichloroethylene) recorded their highest monthly maximas in September 2012. Concentration spikes in monthly average or maximums were attributed to the haze caused by the burning of Sumatran forests. Smokes of the Indonesian forest fires were transported by the southwest monsoon winds to Singapore in September 2012 [7].

Strong Spearman coefficients of $\rho \geq 0.8$ and $\rho \leq -0.8$ were found between 26 pairs of hydrocarbons and 2 pairs of OVOCs respectively. 3 pairs of hydrocarbons had coefficients of determinations $R^2 \geq 0.8$. The explained variations were attributed to overlapping sources between the VOC pairs, such as emissions from motor vehicles and industries, whereas the unexplained variations were related to mutually exclusive sources such as manufacturing of fragrances, dyes and pharmaceuticals. PMF modeling generated 7 source profiles for the modeled hydrocarbons. The base model solution obtained is very stable, has a converged Q(E) with Q(Robust) and Q(true) below one unit of discrepancy and the standardized scale residuals were within ± 3 . Bootstrap analysis was carried out for 100 runs and ≥ 97 bootstrap factors were mapped to the base factors for R^2 correlations > 0.6 . Fpeak rotations were performed between -1 to +1 in steps of 0.1 to avoid rotational ambiguity. An Fpeak value of 0.1 was chosen after the examination of G-space plots in the range of relatively constant Q(E).

Non-cancer and carcinogenic hazards were evaluated by performing a health risk assessment. 16 VOCs were assessed for their non-carcinogenic effects from exposure using hazard ratio (HR_i) calculations, while 5 carcinogens were investigated for their cancerous effects using lifetime cancer risk (LCR_i) calculations for all sample concentrations. The highest mean HR_i (0.112) and LCR_i (9.72×10^{-5}) were both from benzene. 44% of benzene HR_i s falls in the potential level of concern. 37% of benzene LCR_i s are greater than the definite risk value of 10^{-4} with the maximum acquired at

6.41×10^{-4} .

Chapter 4 was devoted to exploring the use of different types of CNTs as sorbent materials for TD-GCMS applications. CNTs are known for their distinctive structures and large surface areas, which can be advantageous for TD. As the adsorption and desorption of gas phase standards were investigated on CNTs in previous studies, the introduction of solution standards into CNT tubes were evaluated to determine the feasibility of the injection method. Due to the necessity of a solvent to prepare the standards for analysis, the adsorption of the solvent on the CNTs is also discussed. The solvent chosen for dilution of the standard compounds was methanol because it was not retained by conventional sorbent materials such as Tenax and Carbopack X. 48 VOCs that were commonly found in the outdoor air in western Singapore were explored by a calibration loading rig injection method coupled with TD-GCMS analysis. No degradation was observed from TGA for all CNTs when heated at 380 °C, ascertaining thermal stability during TD-GCMS analysis and thermal conditioning. Thermal conditioning at 380 °C was carried out before use of the sorbent tubes as well as between uses. The initial conditioning durations of MWCNT and COOH-MWCNT tubes were 13 hours and 16 hours respectively. For SWCNT, sSWCNT and COOH-SWCNT, they were performed at 20 hours, 12 hours and 9 hours, respectively. Conditioning prior to subsequent usage of tubes was carried out at 3 hours for MWCNTs and between 4.5 to 5.5 hours for SWCNTs. Hexane and benzene were identified as artifacts in all CNT blanks and SWCNT had an extra toluene artifact.

Desorption experiments were conducted by introducing 500 ng of the 48 VOC standard solution mix into the 5 CNT tubes. The results obtained suggested that the injection method can be employed for loading compounds with desorption recoveries that are similar in both CNTs and the conventional Tenax/Carbopack X multi-sorbents. In

MWCNTs, peak area ratios ≥ 0.7 were attained for non-polar and aromatic VOCs. Exceptional recoveries of aromatic VOCs was explained by hydrophobic interactions and π - π coupling between MWCNT sorbents and VOC adsorbates which were overcome readily by TD. In addition, this also indicates that the adsorption of aromatic compounds and non-polar VOCs on the MWCNTs are not considerably interfered with by the solvent molecules from the VOC standards solution. There were no prominent differences between the desorption characteristics of the carboxylated and non-carboxylated MWCNTs. A low wt% of $-\text{COOH}$ groups on the functionalized sample might not have been sufficient to significantly alter the adsorption and desorption abilities of the MWCNT. SWCNTs allowed strong desorption recoveries for 25-31 VOCs including arenes, halogenated hydrocarbons, pyridine and furfural. These compounds have peak area ratios ≥ 0.7 and the injection method for standard solution was demonstrated to be viable for those compounds. Aromatic compounds were the mutually common analytes that exhibited exemplary recoveries for SWCNTs and MWCNTs, while the recoveries of alkanes beyond 7 carbons showed the most observable desorption differences between the different CNTs. The low peak ratios of these alkanes detected from SWCNT and COOH -SWCNT sorbents were likely caused by enhanced binding energies on both SWCNTs with increasing alkane carbon chain length.

Breakthrough evaluation was carried out on the nano-sorbent tubes. SWCNTs displayed excellent adsorption capacity for the 48 VOC analytes. All MWCNTs showed irregular dichloromethane (DCM) signals in the back tube (i.e. conventional sorbent tube) during the 4 replicates of the breakthrough experiment. Inconsistent breakthrough of DCM suggests weak retention of the compound. Raman spectroscopy verified the presence of defects on CNTs which possibly behave as high energy adsorption sites for VOCs. MWCNTs had more defects, which could account for DCM breakthrough. Polar

molecules such as DCM and methanol have stronger affinity for defective sites on CNTs due to their polar nature [8]. It is possible that methanol molecules competed with DCM for the adsorption sites at defects and displaced DCM, resulting in DCM leakages. The interference from the solvent molecules was likely to be more of a physical than chemical factor as reactions between solvent molecules with reactive analytes are only likely to occur in acidic aqueous medium. ICPMS analysis detected large amounts of certain transition metal residues such as nickel and molybdenum, which could catalyze reactions between alkenes, alcohols and carbonyls at elevated temperatures. Hence, low peak ratios are possibly attributed to reactions with residual metals rather than interference from the solvent used during the injection method.

CNT sorbents were exposed for 72 hours in a chemistry laboratory environment. Several VOCs were found to adsorb on the CNTs during exposure to air. As there is a likelihood that these retained contaminants may influence reaction yields, take part in chemical reactions or cause side reactions to occur, the findings from the exposure experiment of these materials in ambient air suggests that appropriate procedures should be considered for removing organic impurities in CNTs prior to their applications. Preventive methods for minimizing atmospheric organic contamination during the transfer of CNTs from apparatus are also important. Air samples were obtained by active sampling using the SWCNT tube as it gives the best desorption profiles for the tested VOCs among all nano sorbents. Desorption profiles from sampling were in agreement with functional group observations from the injection of VOC standards into the SWCNT tube. SWCNT had the best potential as a TD sorbent for VOC analysis based on the preliminary data obtained in Chapter 4. The following desirable properties of SWCNT were observed: high thermal stability, high adsorption capacity, sufficient desorption efficiency for VOCs of interest which is attributed to lesser sites of defects.

Future directions in the studies of VOCs in Singapore should include several sampling areas in the east, north, south and central for comparisons of pollutant concentrations within the country. Investigations regarding the limitations of the health risk analysis should be pursued further. As there are missing data (i.e. UR_i s and RfC_i s) for the calculations of HR_i s and LCR_i s for more than 30 compounds of interest, much has to be done to expand on this area. In addition, extensive research is necessary for standardizing RfC_i s and cancer UR_i s between different organizations in environmental and toxicology research. As the evaluation of CNTs in this report is preliminary, more experiments can be carried out to confirm whether catalytic reactions of VOCs can occur due to the existence of transition metal residues in CNTs. This could be evaluated by synthesizing CNT-metal composites with different amounts of metals and using them as sorbents to determine the effects of metals on the desorption recoveries of carbonyls, alkenes and alcohols. Another approach is using CNTs as sorbents after further purification to eliminate most inorganic impurities. Effects of relative humidity, temperature and sampling breakthrough on CNTs have to be verified prior to method developments and validation.

References

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Appendix 1

Chromatograms of 10 L samples collected prior to optimization for qualitative identification of analytes.

Figure A1.1: TIC chromatogram of a 10 L sample collected on 2nd September 2010.

Figure A1.2: TIC chromatogram of a 10 L sample collected on 6th September 2010.

Figure A1.3: TIC chromatogram of a 10 L sample collected on 9th September 2010.

Figure A1.4: TIC chromatogram of a 10 L sample collected on 16th September 2010.

Figure A1.5: TIC chromatogram of a 10 L sample collected on 20th September 2010.

Figure A1.6: TIC chromatogram of a 10 L sample collected on 22nd September 2010.

Figure A1.7: TIC chromatogram of a 10 L sample collected on 19th October 2010.

Figure A1.8: TIC chromatogram of a 10 L sample collected on 20th October 2010.

Figure A1.9: TIC chromatogram of a 10 L sample collected on 21st October 2010.

Figure A1.10: TIC chromatogram of a 10 L sample collected on 22nd October 2010.

Mass Spectrums of 48 target VOC standards used for qualitative identification
1,2,3-trimethylbenzene

Figure A1.11: Mass spectrum of 1,2,3-trimethylbenzene standard.

1,2,4-trimethylbenzene

Figure A1.12: Mass spectrum of 1,2,4-trimethylbenzene standard.

1,3,5-trimethylbenzene

Figure A1.13: Mass spectrum of 1,3,5-trimethylbenzene standard.

1-octene

Figure A1.14: Mass spectrum of 1-octene standard.

2-butanone

Figure A1.15: Mass spectrum of 2-butanone standard.

2-methylheptane

Figure A1.17: Mass spectrum of 2-methylheptane standard.

2-ethyltoluene

Figure A1.16: Mass spectrum of 2-ethyltoluene standard.

2-methylpentane

Figure A1.18: Mass spectrum of 2-methylpentane standard.

3-ethyltoluene

Figure A1.19: Mass spectrum of 3-ethyltoluene standard.

4-ethyltoluene

Figure A1.21: Mass spectrum of 4-ethyltoluene standard.

3-methylpentane

Figure A1.20: Mass spectrum of 3-methylpentane standard.

acetophenone

Figure A1.22: Mass spectrum of acetophenone standard.

benzaldehyde

Figure A1.23: Mass spectrum of benzaldehyde standard.

benzonitrile

Figure A1.25: Mass spectrum of benzonitrile standard.

benzene

Figure A1.24: Mass spectrum of benzene standard.

cyclohexane

Figure A1.26: Mass spectrum of cyclohexane standard.

decanal

Figure A1.27: Mass spectrum of decanal standard.

dichloromethane

Figure A1.29: Mass spectrum of dichloromethane standard.

decane

Figure A1.28: Mass spectrum of decane standard.

ethyl acetate

Figure A1.30: Mass spectrum of ethyl acetate standard.

ethyl ether

Figure A1.31: Mass spectrum of ethyl ether standard.

furfural

Figure A1.33: Mass spectrum of furfural standard.

ethyl benzene

Figure A1.32: Mass spectrum of ethyl benzene standard.

heptanal

Figure A1.32: Mass spectrum of heptanal standard.

hexanal

Figure A1.35: Mass spectrum of hexanal standard.

hexane

Figure A1.37: Mass spectrum of hexane standard.

heptane

Figure A1.36: Mass spectrum of heptane standard.

isoprene

Figure A1.38: Mass spectrum of isoprene standard.

isopropyl alcohol

Figure A1.39: Mass spectrum of isopropyl alcohol standard.

methyl cyclohexane

Figure A1.41: Mass spectrum of methyl cyclohexane standard.

methacrolein

Figure A1.40: Mass spectrum of methacrolein standard.

methylcyclopentane

Figure A1.42: Mass spectrum of methylcyclopentane standard.

methyl methacrylate

Figure A1.43: Mass spectrum of methyl methacrylate standard.

m-xylene

Figure A1.45: Mass spectrum of *m*-xylene standard.

methyl isobutyl ketone

Figure A1.44: Mass spectrum of methyl isobutyl ketone standard.

nonanal

Figure A1.46: Mass spectrum of nonanal standard.

Figure A1.47: Mass spectrum of nonane standard.

Figure A1.49: Mass spectrum of octane standard.

Figure A1.48: Mass spectrum of octanal standard.

Figure A1.50: Mass spectrum of *o*-xylene standard.

phenol

Figure A1.51: Mass spectrum of phenol standard.

pyridine

Figure A1.53: Mass spectrum of pyridine standard.

***p*-xylene**

Figure A1.52: Mass spectrum of *p*-xylene standard.

styrene

Figure A1.54: Mass spectrum of styrene standard.

tetrachloroethylene

Figure A1.55: Mass spectrum of tetrachloroethylene standard.

trichloroethylene

Figure A1.57: Mass spectrum of trichloroethylene standard.

toluene

Figure A1.56: Mass spectrum of toluene standard.

trichloromethane

Figure A1.58: Mass spectrum of trichloromethane standard.

Appendix 2

Monthly Box Plot Analysis

Figure A2.1: Monthly box plots for 1,2,4-trimethylbenzene.

Figure A2.3: Monthly box plots for 1-octene.

Figure A2.2: Monthly box plots for 1,2,3-trimethylbenzene.

Figure A2.4: Monthly box plots for 2-ethyltoluene.

Figure A2.5: Monthly box plots for 2-methylheptane.

Figure A2.6: Monthly box plots for 2-methylpentane.

Figure A2.7: Monthly box plots for 3-ethyltoluene.

Figure A2.8: Monthly box plots for 3-methylpentane.

Figure A2.9: Monthly box plots for 4-ethyltoluene.

Figure A2.10: Monthly box plots for acetophenone.

Figure A2.11: Monthly box plots for benzaldehyde.

Figure A2.12: Monthly box plots for benzene.

Figure A2.13: Monthly box plots for benzonitrile.

Figure A2.14: Monthly box plots for methyl cyclohexane.

Figure A2.15: Monthly box plots for decanal.

Figure A2.16: Monthly box plots for decane.

Figure A2.17: Monthly box plots for ethyl acetate.

Figure A2.18: Monthly box plots for ethyl ether.

Figure A2.19: Monthly box plots for ethyl benzene.

Figure A2.20: Monthly box plots for furfural.

Figure A2.21: Monthly box plots for heptane.

Figure A2.22: Monthly box plots for hexanal.

Figure A2.23: Monthly box plots for hexane.

Figure A2.24: Monthly box plots for isoprene.

Figure A2.25: Monthly box plots for *m,p*-xylene.

Figure A2.26: Monthly box plots for 1,3,5-trimethylbenzene.

Figure A2.27: Monthly box plots for methacrolein.

Figure A2.28: Monthly box plots for methyl isobutyl ketone.

Figure A2.31: Monthly box plots for nonanal.

Figure A2.32: Monthly box plots for nonane.

Figure A2.33: Monthly box plots for octanal.

Figure A2.34: Monthly box plots for octane.

Figure A2.35: Monthly box plots for o-xylene.

Figure A2.36: Monthly box plots for phenol.

Figure A2.37: Monthly box plots for styrene.

Figure A2.38: Monthly box plots for tetrachloroethylene.

Figure A2.39: Monthly box plots for toluene.

Figure A2.40: Monthly box plots for trichloroethylene.

Figure A2.41: Monthly box plots for trichloromethane.

Figure A2.42: Monthly box plots for isopropyl alcohol.

Figure A2.43: Monthly box plots for heptanal.

Positive Matrix Factorization

Factor Optimization

Table A2.1 Summary of Q functions, convergence and residuals of various factors analyzed in the modeling. Q(R) represents the Q (Robust), the quality of fit parameter that excludes outlier points. Q(T) stands for the Q(True) which is calculated for all data points.

Factors	Q(R)	Q(T)	convergence	residuals
3	8866.6	8867.3	Yes	3
4	7188.3	7187.4	Yes	2
5	5898.9	5897.9	Yes	2
6	4807.1	4806.1	Yes	0
7	3893.8	3893.1	Yes	0
8	3316	3315.7	Yes	0
9	2842.2	2841.8	Yes	0
10	2443.7	2443.5	Yes	0
11	2104	2103.7	Yes	0

Table A2.2 R², slope and intercept of observed and predicted concentration scatter plots for 7 factors.

Species	R ²	Slope	Intercept
isoprene	0.92	0.9	0
2-methylpentane	0.87	0.8	0
3-methylpentane	0.82	0.7	0
hexane	0.88	0.9	0
methylcyclopentane	0.83	0.7	0
cyclohexane	0.74	0.6	0
benzene	0.80	0.8	0
heptane	0.69	0.7	0
methyl cyclohexane	0.68	0.6	0
2-methylheptane	0.65	0.6	0
toluene	0.69	0.6	4
1-octene	0.61	0.9	0
octane	0.91	0.9	0
ethylbenzene	0.83	0.8	1
<i>m,p</i> -xylene	0.90	0.8	0
nonane	0.86	0.9	0
styrene	0.80	0.7	0
<i>o</i> -xylene	0.92	0.9	0
3-ethyltoluene	0.85	0.9	0
4-ethyltoluene	0.71	0.7	0
1,3,5-trimethylbenzene	0.66	0.6	0
decane	0.84	0.7	0
2-ethyltoluene	0.92	1.0	0
1,2,4-trimethylbenzene	0.93	0.9	0
1,2,3-trimethylbenzene	0.92	0.9	0

Scaled Residuals for 7 Factors

***Figure to be continued in the next page**

***Figure to be continued in the next page**

Figure A2.44: Scaled residual plots for all VOCs included in the PMF modeling.

Bootstrap Model Runs

Table A2.3 Mapping of boot factor to base factor using a block size of 4 and a minimum R^2 of 0.6.

	Base Factor 1	Base Factor 2	Base Factor 3	Base Factor 4	Base Factor 5	Base Factor 6	Base Factor 7	Unmapped
Boot Factor 1	96	2	0	0	0	0	0	2
Boot Factor 2	0	99	0	0	0	0	0	1
Boot Factor 3	0	1	99	0	0	0	0	0
Boot Factor 4	0	0	0	100	0	0	0	0
Boot Factor 5	0	3	0	0	97	0	0	0
Boot Factor 6	0	0	0	0	0	100	0	0
Boot Factor 7	1	2	0	3	4	0	90	0

Fpeak Model Runs

Figure A2.45: Q(Robust) against Fpeak value.

Figure A2.46: Q(True) against Fpeak value.

VOC concentrations in the source profiles for 7 factors

*Figure to be continued in the next page

Figure A2.47: Concentration of modeled VOCs present in each source profile (in $\mu\text{g m}^{-3}$).