Hybrid Targeted-Nontargeted Analysis of Environmental Air Samples

By

Brittany Marie Argento

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

University of Alberta

Department of Chemistry

Abstract

Air pollution is a global issue which has an impact on various aspects of life with a vast range of pollutants being monitored with different methods. One class of pollutants is the volatile organic compounds and their presence in the air requires improved methods to accurately report the contaminants present. Improved reporting is necessary as current methods are designed to report target compounds, but other volatile organic compounds present in the air can slip through the cracks using these target lists. Therefore, traditional methods have the risk of compounds being missed due to them not being on the target lists. These unknown compounds could also be important in monitoring air quality due to their impact on human health. New methods are needed to determine the presence of both target compounds and unknown compounds through nontargeted analysis. These methods are referred to as hybrid targeted-nontargeted methods and in this work, this is possible using comprehensive two-dimensional gas chromatography. This instrumentation coupled with thermal desorption enables a hybrid targeted-nontargeted method for the analysis of volatile organic compounds in air. Applying this instrumentation to environmental air monitoring can allow for complex samples to be analyzed with more compounds being detected over traditional methods.

Method development has taken place to create a hybrid targeted-nontargeted method for volatile organic compounds in the atmosphere using thermal desorption. Coupling the hybrid method to thermal desorption allows for increased detection of analytes while also simplifying the sample preparation process. Here the separation parameters were optimized as well as conditions for both stages of the thermal desorption process. Furthermore, the sensitivity of the method was examined through limits of detection and limits of quantification. Various applications of the hybrid method have been explored both in outdoor applications and indoor locations to see the variety of volatile compounds which can be present. Overall, a novel hybrid targeted-nontargeted method has been developed for the purpose of air monitoring with the eventuality of being used in an environmental monitoring laboratory. Field applications have shown that there are many compounds which can be present in the air are not on the target list. The work seen in this MSc. thesis has provided a groundwork for a hybrid method for the detection of volatile organic compounds in the air which can be employed for better monitoring of air quality.

Preface

Chapter 1: Introduction

This chapter was written by Brittany Argento with comments from Dr. James Harynuk.

Chapter 2: Development of Hybrid Targeted-Nontargeted TD-GC×GC-TOFMS Method

All the experiments for this chapter were performed by Brittany Argento with guidance from Dr. Paulina de la Mata and Dr. James Harynuk. The chapter was written by Brittany Argento with comments from Dr. James Harynuk.

Chapter 3: Applications of Hybrid Targeted-Nontargeted TD-GC×GC-TOFMS Method

All the experiments for this chapter were performed by Brittany Argento with guidance from Dr. Paulina de la Mata and Dr. James Harynuk. The chapter was written by Brittany Argento with comments from Dr. James Harynuk.

Chapter 4: Conclusions and Future Work

This chapter was written by Brittany Argento with comments from Dr. James Harynuk.

Acknowledgements

To my supervisor Dr. James Harynuk, the skills and support you have taught me throughout my time in your group has been invaluable. I will cherish these for the rest of my life as the impact it will have on my career will be significant. My time in your group has helped me grow as a scientist and as a person.

To my committee members Dr. Ran Zhao and Dr. Wolfgang Jaeger, the feedback and guidance you have provided has been critical to my advancement in the program and has helped me grow.

To Dr. Paulina de la Mata, you have been a role model for me as a scientist which will forever shape me. The lessons you have taught me will stick with me forever and these extend beyond the lab.

To Trevor, Ryan, Kieran, Michael, Sheri, and the other Harynuk group members, we have all been on a journey together and this has included supporting each other and helping each other when needed. Meeting and working with each of you was a gift and it will stick with me for a long time.

To the many staff members including Mike, Ryan, Andrew and Anita, your work was vital to me, both in providing support academically and emotionally on many occasions.

To my friends including Caley, Jordan, and Nicole, you have become an important part of my support circle who helped make sure I enjoyed myself and had fun. You became friends I will cherish forever.

To my father Dan, and to my sister Rachael, I could not have made here without your support growing up. You have shaped me from the start, which has helped me become the person I am.

Saving the best for last, to my husband Nick, I could not have made it without your love and support throughout this journey. The number of times that you took care of me by making sure I took breaks or made sure I laughed are too high for me to count. You have helped carry me through my time as student which means the world to me.

Table of Contents

List of Tables

List of Figures

List of Symbols and Abbreviations

CNS	- Central Nervous System
FID	- Flame Ionization Detector
GC	- Gas Chromatography
GC×GC	- Comprehensive Two-Dimensional Gas Chromatography
LOD	- Limit of Detection
LOQ	- Limit of Quantification
TD	- Thermal Desorption
TOFMS	- Time of Flight Mass Spectrometer
VOCs	- Volatile Organic Compounds
VVOCs	- Very Volatile Organic Compounds
SVOCs	- Semi-Volatile Organic Compounds
OHR	- Optimal Heating Rate
K	- Partition Coefficient
k	- Retention Factor
N	- Theoretical Plate Number
R	- Resolution
α	- Selectivity

Chapter 1 Introduction

1.1 Volatile Organic Compounds and Air Monitoring Methods

Interest in air quality has grown over time due to the impact of air pollution on both the ecosystem and human health.[1–3] Air pollution is when compounds other than naturally occurring gases are present as a result of natural sources or human intervention.[2] Air pollution can be classified in groups such as particulate matter, heavy metals, or volatile organic compounds (VOCs).[2–8] The atmosphere consists of both organic and inorganic compounds which are present in the gaseous phase or as particulate matter.[9] Each of these can have an impact on human health for the individuals exposed, which calls for careful air monitoring to enforce improved air quality guidelines. In this thesis, the focus is on measuring VOCs present in the atmosphere due to their impact on human health and the production of secondary pollutants.[10]

VOCs are classified as compounds with a boiling point less than 250 ℃ at standard pressure according to the World Health Organization.[1] This definition can be broken down further as compounds with boiling points between 0 and 100 ℃ are in the gaseous phase and compounds with boiling points between 100 and 250 ℃ partitioning between liquid, solid or gas surfaces.[1] The term VOC covers compounds which move into the vapor phase when in the air.[4] This covers a broad range of compounds including: aromatic hydrocarbons, aliphatic hydrocarbons, ketones, acids, aldehydes, alkenes, and alcohols as well as halogenated hydrocarbons, sulfur compounds and nitro compounds.[1,10–12] There are a large number of compounds that fall under the VOCs classification and this leads to various potential health risks if an individuals is exposed. The health risks linked to VOC exposure includes irritation of the respiratory system and cancer.[2] The production of secondary pollutants such as ozone leads to additional health effects such as lung inflammation as well as respiration system irritation.[2,11] VOCs can arise from a variety of natural or anthropogenic sources including wildfires, fuels, household products, and landfills.[1,3,4,10–14] Common activities such as painting, printing and even dry cleaning can introduce VOCs into the atmosphere which can create a health risk.[11] This presents a significant risk to all individuals since everyday activities can introduce VOCs to air exposing those in the vicinity.

Secondary VOCs can arise from the primary VOCs introduced into the atmosphere.[11] The lifetimes of these primary VOCs range from a couple minutes to months when introduced to the environment.[1] This allows for the contaminants to undergo transportation or reactions to produce secondary VOCs.[1,15] The production of secondary VOCs requires further monitoring and studies to see their impact on human health. Figure 1.1 shows a simplified scheme of the transport of VOCs after they are emitted from the source.[15] While the primary VOCs are important due to their health impact, the fact that these can lead to the production of other VOCs requires increased monitoring to see these additional compounds. Additionally, other pollutants such as ozone can be produced which creates further risks for human health.[11] The impacts of this on both human health and the environment necessitates the development of new methods to better monitor volatile organic compounds in the amostphere.[16]

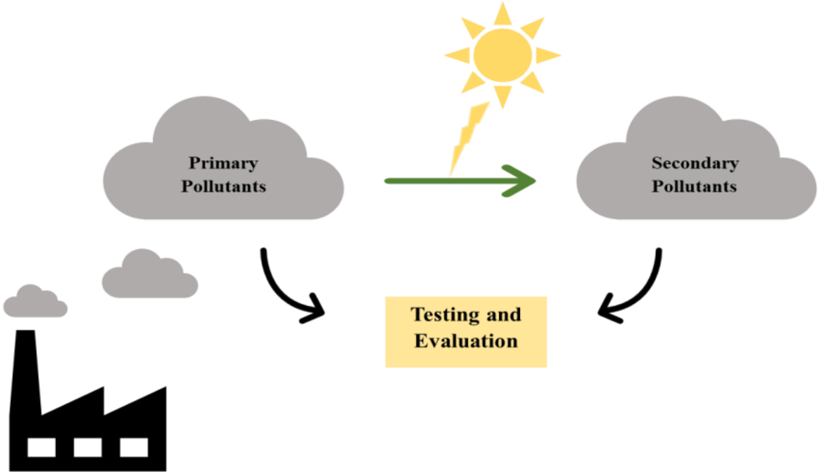
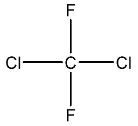
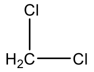
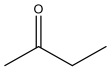
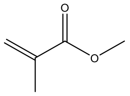
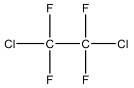
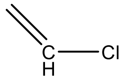
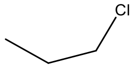
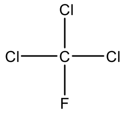
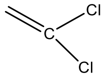


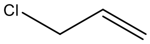
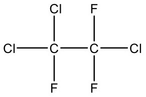
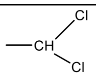
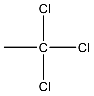
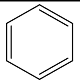
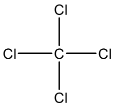
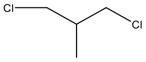
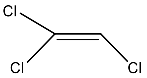
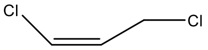
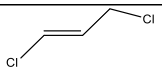
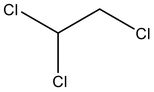
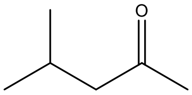
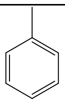
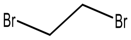
Figure 1.1: Transport of VOCs from the Source to Other Locations adapted from Weitekamp et al.[15]

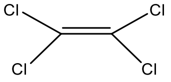
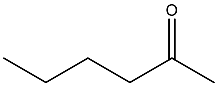
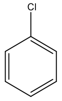
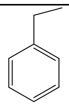
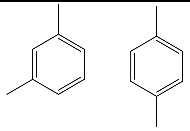
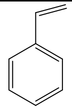
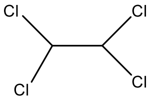
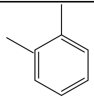
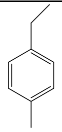
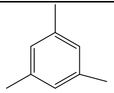
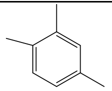
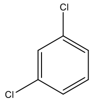
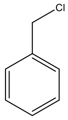
Current methods used today for the detection of VOCs in air were published by government agencies, such as the U.S Enivormental Protection Agency (EPA).[10,17] These methods were published in 1990s with little updates since their publication.[10,17,18] For example, the EPA method for air analysis is the TO-17 method which uses a target list for reporting if any of the 97 target VOCs are present in the air sample.[17,18] Table 1.1 shows an example list of 48 VOCs which are monitored by the agencies such as the US EPA. These compounds are monitored due to the different health risks they present.[11] In targeted methods, only the compounds on the target list are reported which creates a gap in environmental monitoring.[19–21] An example of the problem with targeted lists was seen in Pennsylvania between 2010-2012 with contamination in groundwater.[20] In this case, the groundwater was contaminated from hydraulic fracturing in the area which polluted the water, indicated by the foam found in the water.[20] The source of the contamination was not a part of the target list for water analysis, therefore the cause of the foaming was missed by commercial laboratories.[20] If commercial laboratories are simply basing their work on a targeted list, there is a chance that unknown contaminants will be missed.[21] These unknown VOCs can also have toxic effects and more explorative methods are needed to see them.[21] It is possible that unknown VOCs are present in other environmental samples such as air samples and these would be missed using traditional methods.

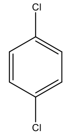
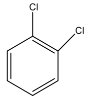
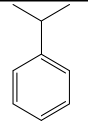
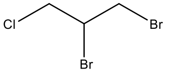
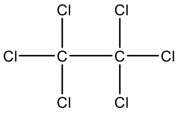
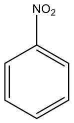
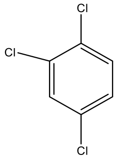
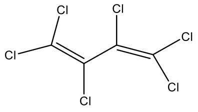
Air samples are complex due to the different compounds present and the VOCs are typically at trace level concentrations which can lead to difficulty interpreting the results of the analysis.[9,22–27] The complexity and trace level concentrations in air samples requires additional steps to ensure the analytes are properly detected during analysis.[24] It is critical that analytical methods for environmental air monitoring are sensitive enough to detect trace level analytes. The combination of the issue with targeted lists and the complexity of air brings forth the need for updated air monitoring methods.[9,19] Due to the limitations of current methods, including problems with identification and quantification, the impact of VOCs has been underestimated.[8,22] Underestimation of VOC levels can cause inaccurate reporting of VOC levels and in some cases VOCs being unreported entirely. Moving to new methods can lead to benefits such as reduced sample preparation and lower analysis time which is perfect for environmental monitoring methods.[22] New methods with the nontarget capabilities can fill the gaps left by current methods. Nontargeted environmental analysis is a necessary tool alongside the target lists in order to be able to detect compounds which have an environmental impact but are not on the target lists.[9] In the Pennsylvania groundwater case mentioned previously, nontargeted analysis was able to find the source of the issue.[20] Llewellyn et al. pointed out that using standard methods may cause compounds to be missed due to these VOCs not being on the list or being at low concentrations.[20] While the previous case shows the need for nontargeted analysis in water analysis, the same can be said for all environmental monitoring. It is possible to see cases like this one in air samples, therefore, the targeted methods are not enough for air monitoring either.

Table 1.1: VOCs of Interest Monitored by the U.S Enivormental Protection Agency

Compounds	Structure	Health Impact	Reference
Dichlorodifluoromethane	 $Cl-\overset{F}{\underset{F}{C}}-Cl$	Asphyxia, cardiac arrest, tremor, cardiac arrhythmias	28
Methylene chloride	 $\overset{Cl}{H_2C}-Cl$	Nausea, numbness, drowsiness, may be carcinogenic	29
Idomethane	H_3C-I	Nausea, vomiting, eye irritation, CNS depression	30
Carbon Disulfide	$S=C=S$	Nausea, headache, convulsions, muscle pain	31
2-butanone		CNS depression, headache, nausea	32
Methyl Methacrylate		Reduced respiratory function, eye irritation	33
1,2-dichloro-1,1,2,2-tetrafluoroethane	 $Cl-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-Cl$	Respiratory irritation, cardiac arrest, asphyxia	34
Vinyl Chloride		Dizziness, headaches, eye irritation, liver damage, liver cancer	35
Methyl bromide	H_3C-Br	Headaches, dizziness, kidney damage, tremors, eye irritation	36
Ethyl Chloride		Dizziness, lack of muscle coordination	37
Trichlorofluoromethane	 $Cl-\overset{Cl}{\underset{F}{C}}-Cl$	Incoordination, tremor, cardiac arrest, asphyxia	38
1,1-dichloroethene		Convulsions, respiratory effects, spasms	39

Methyl chloride	H_3C-Cl	Convulsions, dizziness, coma, nausea, vomiting	40
3-chloropropene		Genetic effects	41
1,1,2-trichloro-1,2,2-trifluoroethane	 $\mathrm{Cl-\overset{Cl}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-Cl}$	Arrhythmia, respiratory effects, psychophysical effects	42
1,1-dichloroethane		Cardiac arrest, CNS damage	43
1,1,1-trichloroethane	 $\mathrm{-\overset{Cl}{\underset{Cl}{C}}-Cl}$	Respiratory issues, vomiting, diarrhea, nausea	44
Benzene		Carcinogenic, headaches, confusion, can cause amenia	45
Carbon Tetrachloride	 $\mathrm{Cl-\overset{Cl}{\underset{Cl}{C}}-Cl}$	Dizziness, nausea, vomiting, seizures, coma, concentration loss	46
1,2-dichloropropane		Liver damage, kidney damage, dizziness irritation	47
Trichloroethene		Carcinogenic, liver damage, confusion, headache	48
Cis-1,3-dichloropropene		Dizziness, eyes, skin, and respiratory system irritation	49
Trans-1,3-dichloropropene		Dizziness, eyes, skin, and respiratory system irritation	49
1,1,2-trichloroethane		Animal studies: effects on liver, kidneys, CNS	50
Methyl Isobutyl Ketone		Eye irritation, headache, dizziness	51
Toluene		Nerve damage, confusion, liver, or kidney damage	52
1,2-dibromoethane		Damage to liver, kidneys, heart, spleen, irritation	53

Tetrachloroethene		Respiratory system irritation, behavior changes	54
2-hexanone		Numbness, weakness, tingling in hands and feet	55
Chlorobenzene		Drowsiness, irritation, poor coordination	56
Ethylbenzene		Respiratory irritation, eye irritation, dizziness	57
m,p-xylene		Eye, nose or skin irritation, headaches, confusion	58
Styrene		Respiratory effects, CNS disfunction	59
1,1,2,2-tetrachloroethane		Liver damage, respiratory irritation, headaches	60
o-xylene		Eye, nose or skin irritation, headaches, confusion	58
4-ethyltoluene		Potentially fatal if inhaled	61
1,3,5-trimethylbenzene		Dizziness, nausea, vomiting, confusion, headache	62
1,2,4-trimethylbenzene		Vomiting, headache, nausea, poor coordination	63
m-dichlorobenzene		Little known but potentially irritation, dizziness, headaches	64
Benzyl Chloride		Weakness, headache, irritability	65

p-dichlorobenzene		Eye, skin, and throat irritation	[66]
o-dichlorobenzene		Kidney damage, irritation, skin blisters	[67]
Cumene		Headaches, dizziness, drowsiness, unconsciousness	[68]
1,2-dibromo-3-chloropropane		Eye irritation, kidney effects, CNS effects	[69]
Hexachloroethane		CNS depressant, skin and liver irritation	[70]
Nitrobenzene		Decreased oxygen to tissues, headaches, liver damage	[71]
1,2,4-trichlorobenzene		Animal studies: lung irritation	[72]
Hexachlorobutadiene		Animal studies: respiratory effects	[73]

1.2 Volatile Organic Compounds and their Risks

Air is complex which presents many difficulties in sampling and VOCs are just one example of the pollutants present in the atmosphere.[1,74] Clean air consists of gases which are naturally present such as oxygen, nitrogen, and argon; however, in many cases there are other compounds present such as VOCs which can harm plants, animals or people.[1,2] VOCs are pollutants that are generally in the gas phase in the air, however, there is the risk that these can be present even when there is no visual indication of pollution.[75] Many activities people do every day increase the levels of VOCs in the air in addition to natural VOC sources such as plant life producing terpenes.[76] Waste storage, forests emissions, vehicles, as well as various household products lead to VOC production.[4] Products such as smoking tobacco, paints, cosmetic products, and building materials are just some examples of products which off gas VOCs.[77] A significant portion of the airborne VOCs are from biogenic sources and VOCs emission is influenced by the local environment such as the plant life, industries, and climate activity.[12] The wide range of potential sources can introduce hazardous VOCs in both indoor and outdoor locations presenting risks to the individuals exposed.

As referenced earlier, governmental agencies already have a list of target VOCs which present a risk to human health. Some of these compounds of interest include benzene, 1,3-butadiene and vinyl chloride due to their carcinogenic nature.[1] Benzene and its derivatives toluene, ethylbenzene, and the xylenes (ortho, meta and para) are normally denoted as BTEX.[1] The BTEX compounds are a significant portion of the airborne VOCs.[1] Benzene, for example, is of interest due to its health effects and example sources include the fuel industry and cigarettes.[45] Benzene has been shown to be genotoxic due to animal research showing DNA damage and it also has led to an increase in leukemia in adults causing its classification as a carcinogen.[5] BTEX levels in highly industrial areas are elevated, however, levels are also elevated in large cities as a result of high traffic due to BTEX being present in gasoline.[1]

Another VOC of interest is methylene chloride or dichloromethane (DCM) which is normally found in paint strippers and is commonly used a solvent.[78] Another VOC, 1,3-butadiene, is a component of rubber as well as gasoline with the sampling and monitoring of this compound having been explored as it is a common pollutant, though there has been difficulty monitoring it as a result of its stability.[79–82] 1,3-butadiene undergoes reactions when in the atmosphere giving off products which also can have negative health effects.[82] The 1,3-butadiene degradation products are not regulated despite one of these compounds (1,2,3,4-diepoxybutant) being more carcinogenic than 1,3-butadiene.[82] In many cases, degradation products from VOCs are a greater risk to human health compared to the primary VOC.[83] These hazardous air pollutants can cause various different health effects such as damage to the immune system, neurological damage, reproductive issues, developmental problems and respiratory system damage.[84] While these VOCs may come from a variety of sources, the health risks of these compounds can be severe. Air pollution, including VOCs, can enter the body through two main routes, inhalation and ingestion, but exposure through the skin is a minor route that pollutants can take into the body.[3,6,85] Kampa and Castanas discussed the various health effects of different air pollutants, and here they listed several health effects such as breathing problems, cancer, skin irritation, nausea and damage to the immune system.[3] Rumchev et al. looked specifically at VOCs, showing that they are linked to: respiratory issues, allergy problems, sensory problems, and irritations as well as the earlier mentioned carcinogenic properties.[77] The extent of the health effects VOCs can have on an individual presents the need for new air monitoring methods in order to better detect these pollutants.

There is another issue with the presence of VOCs in the atmosphere, in addition to the various health impacts of VOCs alone. The additional issue with VOCs in the air is that when they are in the presence of sunlight and NO/NO_2 (NO_x), ground level ozone is produced.[3,8,86,87] While in the stratosphere ozone removes the harmful UV light, on the ground level ozone is an air pollutant which is harmful to both human health and plant life.[4,86] The production of ground level ozone is a significant risk presented by the presence of VOCs which requires improved monitoring. Ozone is attributed to worsening asthma and other respiratory problems as well as reducing photosynthesis in some plants which inhibits plant growth.[88,89] Furthermore, ozone can travel a large distance from the point of origin and the half-life for ozone is long.[4] In particular, the half-life of ozone in the summer months is 1-2 weeks while in the winter months the half-life of ozone is increased to 1-2 months.[4] Ozone exposure leads to the constriction of airways thus air will be trapped in the alveoli causing shortness of breath as well as contributing to chronic obstructive pulmonary disease (COPD).[88] Extended exposure to ground level ozone can lead to further asthma issues and higher concentrations of ozone can cause abnormal lung function as well as lasting harm.[88] For the ecosystem, there can be a loss of species and plant exposure to ozone can have negative impact on the environment.[89] The significant impact VOCs have on human health upon exposure together with their contribution to the production of secondary pollutants presents the need to carefully monitor airborne VOCs.[8] The dual risk of VOCs in the ambient air to human health and the environment necessitates the development of a new method to better monitor these compounds.

1.3 Air Sampling for Environmental Monitoring

Sampling is the most critical aspect of the analytical process and sampling for air monitoring has evolved over time. The goal of the study will dictate a type of sampling used and many of the methods used today include canisters, sampling bags and sorbent tubes.[90] This is in addition to the online sampling methods which enables air to be analyzed in real time for VOCs in a variety of applications.[90] Two types of air sampling are active sampling and passive sampling, and each has its own purpose.[91] Active sampling is used in this work for a range of applications and there are a few ways to perform active sampling. Canisters and sampling bags are two examples of samplers which can be used in active sampling and these can have either fixed or variable volume.[92]

Table 1.2: Summary of Air Sampling Methods Used for Environmental Air Monitoring

Sampling Method	Analyte Type	Reusability
Sampling Bags (Ex. Tedlar Bags)[90]	VVOCs, VOCs	No
Steel Canisters[90,91]	VVOCs, Permeant Gases, VOCs	Yes
Passive Samplers[90]	VOCs	Sampler Dependent
Sorbents Tubes (Solvent Desorption)[93–96]	VVOC	No
Sorbents Tubes (Thermal Desorption)[93,94]	VVOC, VOCs, SVOCs	Yes

Steel Canisters

Tedlar Bags

Thermal Desorption Sorbent Tubes

Figure 1.2: Image of Common Air Sampling Devices Including Steel Cannisters, Tedlar Bags and Sorbent Tubes

Table 1.2 gives a summary of some methods for sampling the atmosphere for contaminants. There is some overlap between the classes of VOCs that can be sampled by the different methods therefore the selection of the sampling method is up to the analyst. Users must consider the goal of the study and the cost of the analysis as well as size of sampling apparatus. This is because while there is overlap between the VOCs that can be collected, the different sampling methods can not be used in same applications. Each method requires different considerations for planning such as transport, power supplies and sampling flow rates as well as other parameters. Figure 1.2 shows examples of three of the samplers mentioned in Table 1.2. The cannister and Tedlar bag shown in Figure 1.2 are examples of whole air sampling devices that are commercially available.[97,98] Figure 1.2 also includes thermal desorption sorbent tubes which collects of VOCs via a sorbent.[90] Care and maintenance of the sampling equipment needs to also be considered as well since sampling containers such as steel canisters may require different maintenance steps. Sampling bags also require care as there is risk for rupture of the bag and they can not be easily reused.[90,95] Stainless steel canisters require deep cleaning between uses as well as purging in order to ensure the sampling device is clean before a new sample is collected.[90] This can be considered a major disadvantage as this would be a very time consuming step in order to prepare one canister for sampling. Preparation time is significant consideration as this could impact the number of samples that can be collected as well as the timeline of the study.

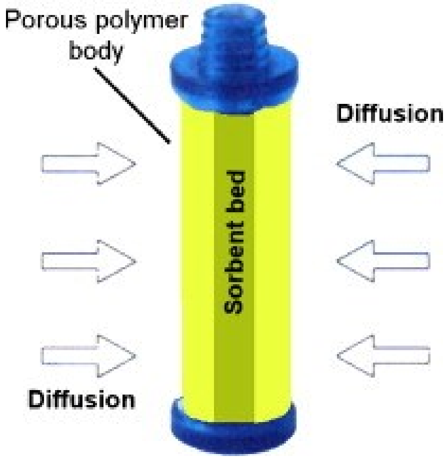


Figure 1.3: An Example of a Passive Sampler - Radiello Sampler[1]

Passive samplers are used for time weighted average sampling and operate on the basis of diffusion.[99] There are passive samplers which can desorbed using solvent desorption which can not be reused, however there are also passive samplers used with thermal desorption which can be reused.[90] Therefore as mentioned in Table 1.2, the reusability of the passive sampler depends on the sampler being used in the analysis which leads to careful consideration for the analyst. An example passive sampler is shown in Figure 1.3, in particular a Radiello sampler is shown and the direction of diffusion for this sampler is indicated.[90] Radiello samplers are one example of passive samplers which can be used for air sampling. Here the passive sampler removes the need for sampling pumps but there is a risk of VOCs diffusing off the sampler.[90] While there are several advantages to the passive samplers, they are generally not used for short term monitoring.[95]

Sorbent sampling is a mode of collecting VOCs which provides versatility due to the wide range of sorbents available and number applications they can be utilized in. The original sorbent sampling device was a glass tube packed with charcoal which was used for years as a way to sample high concentrations of VOCs.[10,90,100] The charcoal tubes were desorbed using a solvent, commonly carbon disulfide as it is very volatile with a low response on flame ionization detectors (FIDs).[90,100] While this method of sample preparation worked in the early years of environmental air monitoring, over time significant disadvantages of solvent desorption can be

---

[1] Reprinted from Journal of Chromatography A, 1217/16, Elizabeth Woolfenden, Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air: Part 1: Sorbent -based air monitoring options, 2674-2684, Copyright (2010), with permission from Elsevier.

seen. As indicated in Table 1.2, sorbent samplers used for solvent desorption methods can present an increase in sampler cost as they are single use. Woolfenden pointed out in her discussion on sorbent sampling that solvent desorption presents issues such high detection limits, interference on a mass spectrometers and health hazards when using solvents such as carbon disulfide.[90] High detection limits and interferences are problems in analytical chemistry as compounds can be missed during analysis. Health hazards from carbon disulfide present issues during sample preparation and during solvent disposal which then creates an issue for the environment.[90] Moving to remove a health hazard from the sample preparation process is important so laboratories can protect their analysts from exposure to hazardous substances. Furthermore, environmental monitoring facilities should take care to not introduce more contaminants to the environment. Then next stage of sorbent sampling is using them in process called thermal desorption (TD) which combines sample collection with the sample preparation process.[94] The problems with solvent desorption are essentially removed from the analytical process when thermal desorption is employed in its place.[90] The improvement in parameters such as detection limits is very appealing to analysts as compounds can be detected at lower levels.

Thermal desorption is an automated process where the sorbent is heated in a flow of inert carrier gas.[90] The carrier gas flow is reversed compared to sampling flow, then the sample is transferred to the gas chromatograph.[90] This brief summary of the process of thermal desorption presents the reason for the benefits of this method which is that the sorbent is heated. This allows for the analytes to be removed from the sampling medium without any interferences from solvent or health hazards to the analyst.[94] This process enables all of the sample to be introduced to the gas chromatograph for analysis compared to the small volumes injected for solvent desorption which allows for more sensitivity.[90,94] Using thermal desorption will also prevent dilution of the sample which occurs with solvent desorption is used.[101] Complete transfer and removal of dilution provides better detection of compounds due to increased sensitivity thus leading to improved environmental monitoring. These benefits make thermal desorption a powerful tool to be used with air monitoring methods. Another major benefit is that samplers for thermal desorption are reusable up 100 cycles thus the sampling cost is reduced.[94] This is indicated in Table 1.2 and the reusability of the samplers can make up for the initial cost of the thermal desorption unit. Modern instruments use a two stage desorption process and Figure 1.4 shows an two-stage thermal desorption unit from Markes International's thermal desorption unit manual which uses the Peltier cooling process.[90,102] The two stage desorption process begins with the first stage involving a sorbent tube and the second stage using a focusing trap which is packed with sorbent.[90] In the first stage the sorbent tube is loaded into the tube oven for desorption and then the VOCs are collected on to the focusing trap.[90] In the second stage of desorption, the focusing trap is desorbed causing the sample to be injected into the gas chromatograph for analysis.[90] Both stages use a reversed flow of carrier gas to desorb the analytes from the sorbents.[90] This design allows for an increase in sensitivity as after each stage the sample is desorbed in smaller volumes of carrier gas with focusing trap desorption injecting a between 300-400 µL of carrier gas.[90,94] For this instrumental design, the two stages of desorption combines with the complete sample transfer mentioned earlier which increases the sensitivity of the method providinh more reason to move to this instrumentation. Thermal desorption has advanced over the years and has continued to grow in use for environmental air monitoring.

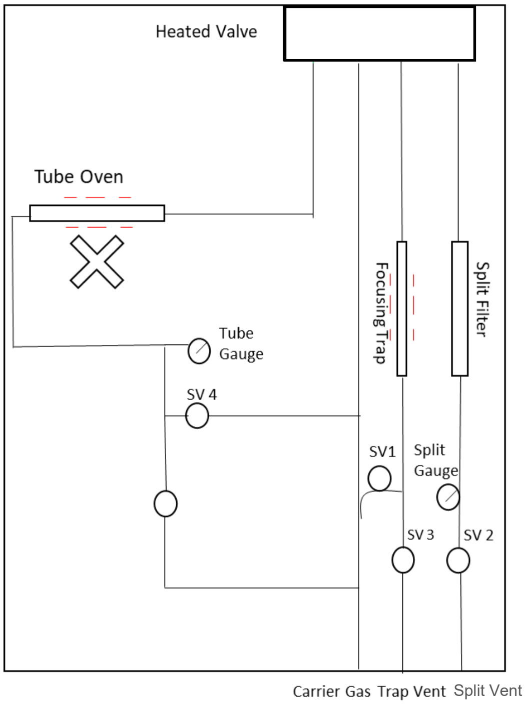


Figure 1.4: Thermal Desorption Unit Schematic Showing Two Stage Desorption adapted from Markes International Manual[102]

One of the earliest examples of thermal desorption for environmental air monitoring was seen in 1979 where Brown and Purnell examined the chromatographic properties of the adsorbent, Tenax-GC.[103] Even then the benefits of thermal desorption were seen with Brown stating that it offered better sensitivity as well as the removal solvent peak from the chromatogram.[103] The lack of a solvent peak can allow for more compounds to be seen. This benefit being shown in 1979 laid the groundwork for future instrumental development which gave ample reason to move from solvent-based methods. The optimal flow rate for sampling with sorbent tubes in thermal desorption was determined to be 50 mL/min due to the number of theoretical plates.[103] In terms of the chromatographic resolution seen with TD, in order to prevent significant band broadening and loss of resolution, a second trap is needed.[104] With single stage desorption, the milliliters of gas needed to desorb the sample can not be used with capillary gas chromatography, as a result of this, there was an attempt to combat this with cryofocusing.[94] However, cryofocusing presents several concerns such as ice blockage and higher cost of analysis.[94] These disadvantages of single stage desorption lay out the reasoning for the move to two stage desorption. The reason for this is that in order to desorb the sample with good chromatographic resolution, the volume of carrier gas should be small and to do this two stage desorption is used as it allows for better resolution.[104] Looking at the technology available today, there are many advantages of TD which includes full sample transfer, high desorption efficiency, automation, reusable samplers and removal of interferents such as water.[94] This technology eliminates essentially all of the problems with solvent-based methods and moving to thermal desorption methods would aide environmental monitoring laboratories in improving their analyses.

There are a couple of designs of thermal desorption instrumentation can be used with one of the common designed produced by a company called Markes International. This design follows the two-stage desorption method described previously and a process called Peltier cooling is used to cool the focusing trap.[90] This allows for the VOCs to be trapped without the use of expensive cryogens.[94] The removal of cryogens is a significant reduction in the cost of analysis which is present in this design of the thermal desorption unit. The focusing trap is desorbed at heating rates up to 100 °C/s, once again using a reversed flow of inert carrier gas.[90] The reversal of the carrier gas flow allows for the usage of multisorbent tubes and multisorbent focusing traps as it prevents low volatility analytes from being trapped on strong sorbents.[93] Another benefit of the reversal of the carrier gas flow is that less volatile compounds are easily removed from the sampling end of the sorbent tube.[105]

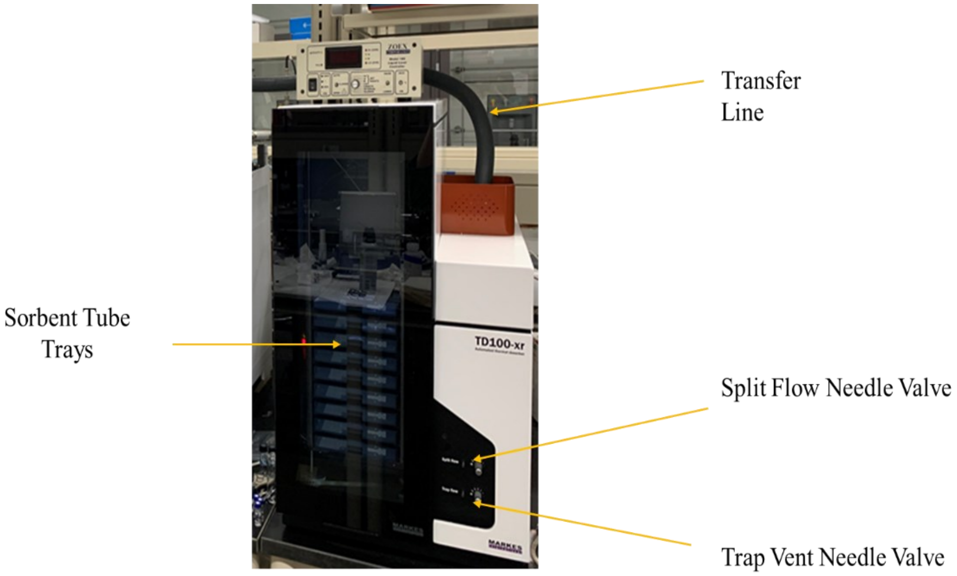


Figure 1.5: Picture of the Markes International TD 100-xr Used in This Work

Figure 1.5 shows an image of the TD 100-xr two stage thermal desorption unit developed by Markes International which uses the schematic shown in Figure 1.4. This instrument was used in this thesis for the thermal desorption of samples and standards. Additional features highlighted in Figure 1.5 include the transfer line which is used to introduce the sample to the gas chromatograph for analysis. The split flow needle valve and trap vent flow needle valve are also shown, and these are used to set the split flow rate and the flow rate for the tube desorption. A flow meter is needed to set the flow rate using these needle valves. Figure 1.5 also shows the sample trays where the sorbent tubes are placed to be loaded into the unit for desorbed. Up to 100 sorbent tubes can be loaded into the unit to be automatically desorbed for analysis. The unit shown in both Figure 1.4 and Figure 1.5 allows for streamlined sample preparation due to the automation.

When developing TD-GC methods, it is important to carefully select the temperatures (for both sorbent tube desorption and focusing trap desorption) as well as the flow rates for desorption and desorption time.[94] The need for a split or splitless desorption needs to be considered and modern instrumentation allows for splitting at both stages of desorption.[94] TD instruments include a purge/pre-purge step which allows for the removal of interferents such as water from the sample and sends them to vent.[94] It is important to consider the length of purge time as if an improper time is selected, the results may be negatively impacted due to effects it may have on calibration standards.[106]

The works by Brown and Coker set the ground work for the usage of TD in environmental analysis but this technique has grown and become more widespread in the analytical air monitoring community.[103,104] Indoor air monitoring was done in 1992 with TD-GC-MS and validated for a targeted analysis which had LOD values less than 4 ng/sample and LOQ values less than 12 ng/sample.[107] More recently the U.S EPA has implemented TD-GC-MS in their most recent air monitoring methods after using stainless steel air canisters in previous methods.[17,18] A 1999 study in the UK was able to show that TD enabled detection limits of 0.1-0.2 ppb with low concentrations of 0.16-1.59 ppb for aromatic and non-aromatic hydrocarbons where measured in Leeds air.[108] It has been shown through the use of multiple sorbents in a single tube that a wide range of VOCs can be analyzed in a single analysis.[109] Pankow et al. showed the detection of 87 VOCs from 10 different classes at detection limits between 0.02-0.06 ppbv with the use of the multiple sorbents.[109] Several works have been able to show the advantages in sensitivity provided by thermal desorption through lower limits of detection. Researchers have employed TD-GC-Sulfur Chemiluminescence Detection for the analysis of volatile organic sulfur compounds and this was specifically applied to sewer emissions showing usage of thermal desorption beyond VOCs.[110] Indoor air monitoring has been performed with TD-GC×GC coupled to high resolution TOFMS which showed a connection between human health and the chemicals present in indoor air during a study related to sick building syndrome.[111,112] Thermal desorption has seen a widespread usage in the field of environmental air monitoring and the sorbent tubes being used in sampling process play a significant role in the experiment planning.

1.3.1 Thermal Desorption Sorbent Selection

There are several benefits of sorbent tube sampling over methods such as cannisters or Tedlar bags. One such benefit is that sorbent tubes allow for larger sample volumes to be collected while also being easy to use.[90,113] To ensure that the sampling needs are met for the study, the proper sorbent needs to selected, therefore there are several factors for an analyst to consider.[93] These factors are strength of the sorbent, inertness, level of hydrophobicity, artifact levels, thermal stability and the mechanical strength.[93] The chosen sorbent needs to be able to collect the analytes of interest while allowing them to be desorbed at a temperature allowed by the sorbent.[90,94] The volatility range of the analytes needs to be carefully considered in order to select the correct sorbent and commercially there is a range of weak, medium and strong sorbents to choose from.[93] Here the goal of the study needs to be carefully considered to select a sorbent that covers the range of analytes of interest. Reactive compounds are an issue with sorbents which have active sites while other sorbents can absorb water which is a major issue if not properly handled.[93] Thermal stability varies for different sorbents with some have a temperature limit as low as 225 °C and others having higher temperature limits around 400 °C.[93] It should be noted that sorbents used for solvent desorption can not be used for thermal desorption due to their high surface activity which requires high temperatures for desorption thus leading to degradation.[100] Similarly, sorbents for thermal desorption can not be used for solvent desorption due to the sorbents not being able to handle large volumes and high concentrations.[100] There are three main classes of sorbents which are used for TD in ambient air sampling: porous polymers, graphitized carbon blacks and carbon molecular sieves.[93,95,96,114]

Looking first at the porous polymers which range between weak to medium in strength and are hydrophobic in nature.[96,114] These are either cross linked linear, homogenous cross linked and heterogenous cross linked polymers created from a mixture of monomers in an inert solvent.[114] Examples of porous polymers used in TD work include Tenax TA, Chromosorb 106, Chromosorb 102, Porapak N and Porapak P.[96,114] Tenax TA, diphenyl-*p*-phenylene oxide, is a common sorbent which has the benefits of having low background levels, the ability to handle high temperatures up to 350 °C and is hydrophobic.[93,100] Tenax TA, a very weak sorbent, is typically used for the collection of aromatics, polyaromatic hydrocarbons as well as polar species of low volatility.[96,105] Despite Tenax TA being a good sorbent, artifacts can form over time or when in the presence of ozone.[114] While it is a commonly used sorbent which works well for compounds with boiling points between 80 – 200 °C, it is not optimal for sampling high volatility alkanes, alkenes or haloalkanes.[10] Other porous polymers, such as Chromosorb 106 and Porapak N, are available for more polar compounds such as oxygenated VOCs but these sorbents have low thermal stability which limits their usage.[96]

The next type of sorbent is the graphitized carbon blacks and these are formed at temperatures of 270°C from soot produced from fuels.[114] The graphitization process impacts the surface area of the sorbent, which gives an estimation of the sorbent strength, therefore greater graphitization leads to weaker sorbents.[114] It is important to note that graphitized carbon blacks are not inert thus reactive compounds should not be sampled onto these sorbents due to the compounds reacting with the sorbent.[93] These sorbents do have the benefit of being relatively hydrophobic, having low artifacts, and high thermal stability with maximum temperatures around 400 °C.[93] Lastly, there are the carbon molecular sieve sorbents which are polymers such as poly(vinylidene chloride) and poly(vinyl chloride) which are pyrolyzed around 180 °C.[114] Carbon molecular sieves have high thermal stability but these sorbents are not hydrophobic and are used for the collection of very volatile compounds.[96,100] Also, carbon molecular sieves are typically used in combination with other sorbents due to their high strength.[96] Unless very volatile analytes are to be targeted in the analysis, then the carbon molecular sieves are used in combination with other sorbents in multisorbent tubes.[100] It is important to understand that there is no sorbent or method which can cover the full range of VOCs of interest.[10] This is related to how each sorbent only has a certain range of VOCs that can be collected.

In the cases where there is a wide range of volatility to be covered, a single sorbent is not enough and in these cases more than one sorbent can be packed inside a multisorbent tube.[90,93,100] Here the sorbents are packed from weakest to strongest to prevent low volatility compounds from becoming trapped on strong sorbents.[96,100] This allows compounds to be collected in order of low volatility to high volatility due to the design of multisorbent tubes.[100] Furthermore, the multisorbent tubes allow for a more diverse range of compounds to be sampled at a single time as proper selection of sorbents makes it possible to sample nonpolar and polar compounds at the same time.[115] As there is no universal sorbent, a multisorbent tube is the only way for analytes of various different volatilities to be collected at the same time.[90,114] Packing sorbents of different strengths into a single thermal desorption tube enables a wider range of VOCs to be sampled at a single time. These multisorbent tubes have grown in popularity over the years and methods published by governments have employed them as well.[100] Correctly selecting the sorbent for the experiment is critical for the sampling process and improper selection can be detrimental to the results.[94]

1.3.2 Sampling Considerations for Air Sampling using Thermal Desorption

As with any study, air sampling must be performed carefully to obtain representative samples. Active sampling is a more flexible option which involves passing air through the stainless steel or glass tube packed with sorbent through the usage of an air pump.[90,96,100,116] The sampling time for active sampling can be minutes or even hours and the air pumps pull the air at a calibrated flow rate.[100,116] The published methods from governmental agencies use active sampling due to the fact that the equipment can worn by an individual.[96,113] Active sampling enables the technician to control both the sample time and the sampling rate.[113] An important note is that this mode of sampling enables large volumes of up to 150 L to be sampled with flow rates ranging from 10-200 mL/min.[90,96,113] The sampling time and pump flow rate are related as the higher flow rates, for example 200 mL/min, are used with quite short sample times such as 15 minutes.[90] Less volatile compounds can also be sampled at flow rates as high as 500 mL/min with no impact on the performance.[93] When preparing for active sampling, it is critical to avoid breakthrough, which is the term for when analytes exit the sorbent bed during sampling, as this creates a less representative sample.[90,100] One of the EPA definitions of breakthrough is the volume of constant analyte concentration which can be sampled before 5 % of the analyte concentration exits the sorbent tube at the opposite end.[17] The second EPA definition is when two sorbent tubes are coupled together and breakthrough occurs when the amount on the second sorbent tube is 5 % of the total amount of analyte on both sorbent tubes.[17,100] An important note to make is that multisorbent tubes can only be used with active sampling as only the sorbent on the sampling end of the sorbent tube is exposed to the sampling environment.[93] Whether single sorbent tubes or multisorbent tubes are used, parameters such as flow rate and sampling time need to considered prior to sampling.

1.4 Gas Chromatography

Once the samples are collected, these complex mixtures need to be analyzed to determine their composition. Mixtures of compounds can be separated to determine the identity and amount of the components present in the sample using chromatography.[117] Gas chromatography (GC) is one of the first separation methods that was developed and this is a commonly used technique used for analyzing environmental samples for organic contaminants.[14,26,87,118] In GC, the separation of volatile components takes place as the analytes move through the column by the gaseous mobile phase (an inert gas such as He, N_2, or H_2) while partitioning into the polymer stationary phase. The separation is dependent on the partition coefficient (K), which is the relationship between the concentration of the analyte in mobile phase and the concentration in the stationary phase.[117,119] Another parameter impacting the separation is the retention factor (k)

which determines the amount of analyte in each phase using the retention time of the analyte and the retention time of unretained compound (dead time).[117,119] Many factors impact how long an analyte is retained in the stationary phase such as the structure of the analyte, stationary phase structure, temperature and pressure. Any change in these factors will lead to a change in the K or k values causing a change in the retention of the analyte.[120] The resolution of various analytes can be determined using the Pernell equation:

$$R = \frac{\sqrt{N}}{4} \times \frac{k}{k+1} \times \frac{(\alpha - 1)}{\alpha}$$

Equation 1.1: Pernell Equation for Chromatographic Resolution

Here the factors affecting the resolution are given, these include the separation efficiency (N), degree of retention (k) and the selectivity (α) which gives the degree of separation between two peaks.[120]

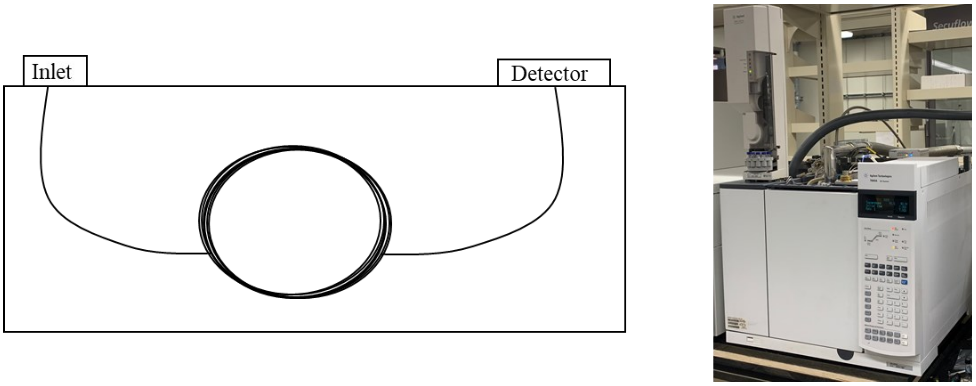


Figure 1.6: Gas Chromatograph Schematic (Left) and a Modern Analytical Gas Chromatograph (Right) for One-Dimensional Gas Chromatography

Modern analytical GCs use open tubular capillary columns for separations due to their efficiency and these columns are typically between 5 -100 m in length, 0.1- 0.8 mm in inner diameter with a stationary phase film thickness between 0.1 - 5.0 µm.[121–123] Figure 1.6 shows the schematic of a capillary GC and an image of an Agilent 7890 A gas chromatograph which are used in analytical GC separations. Following the schematic in Figure 1.6, the sample enters at the inlet before being introduced into the analytical column where separation takes place before components reach the detector. The GC shown in Figure 1.6 has electronic controls for flow rate and temperature using the keypad on the instrument giving the analyst easy control. The selection of the stationary phase is critical to ensure a good separation and there is a wide range of commercial columns available with several developed for specific applications.[121,122] Stationary phases using polydimethylsiloxanes allows for separations based on analyte volatility due to dispersive interactions, then replacing the methyl groups in this phase with phenyl groups change will the separation mechanism.[121] In addition to these stationary phases, there are additional polar phases which contains functional groups such as cyanopropyl and trifluoropropyl groups as well as a polyethylene glycol phase (wax) for more selective separaions.[121,123] In terms of detectors, several different detection systems have been used in GC including the FID and electron capture detectors as well as mass spectrometric detectors which gives the benefit of structural information.[123,124] For environmental applications, the column dimensions are commonly 10 – 60 in length, with inner diameters of 0.1 – 0.32 mm and film thicknesses between 0.1 – 0.5 μm.[118] Various stationary phases can be used for different organic pollutants including: 5% phenyl polydimethylsiloxane, cyanopropylphenyl polydimethylsiloxane, and polyethylene glycol.[118] Despite the wide usage of gas chromatography in environmental analysis, it may not be enough to adequately separate these samples due to the complex nature of the sample.[8]

1.4 Comprehensive Two-Dimensional Gas Chromatography

To separate highly complex environmental samples, particularly those consisting of organic compounds at trace levels, methods with increased separation power are needed. An analytical technique with increased separation power that is commonly used is comprehensive two-dimensional gas chromatography (GC×GC).[8,9,14,19,27,117,125–128] The concept behind this methodology was first theorized by J.C Giddings in 1984 as it becoming known that traditional GC could not handle more complex samples.[129] The first case of this instrumentation being used was in 1991 by Liu and Phillips where a prepared hydrocarbon mixture and coal liquids were analyzed.[130] Here the sample is introduced into the first dimension column for one degree of separation, then the eluent enters the modulator to be trapped, focused and reinjected into the second dimension.[125,131]Further separation takes place in the second dimension before the analytes reach the detector which is typically the FID or TOFMS.[125,131] Here the results have two retention times which are useful in identification of compounds using standards which was highlighted in Liu and Phillips' 1991 work.[130] This is known as a "comprehensive multidimensional separation" as each fraction of the entire sample experiences both dimensions of separation and the first dimension separation is persevered throughout the process.[117,125,132] Here the two columns have different stationary phases which enhances the separation power leading to several key benefits: increased selectivity, increased peak capacity and pattern identification of homologous compounds.[14,117,125,131]

In GC×GC, the first dimension column has similar dimensions to the columns used in traditional one dimensional GC separations with lengths between 15-30 m, commonly the inner diameter is 0.25 mm and the film thickness lies between 0.25-1.0 µm.[117,132] The second dimension column is typically a short column with a narrow diameter, typically 0.25 mm is used, and a thin film thickness between 0.1 and 0.25 µm to ensure a fast separation.[117] The sample is reinjected during the modulation period and ideally the second dimension retention times are less than the modulation period but this places limits on the length of the second dimension column in order to have a fast separation.[117] The heart of this technique is the modulator which enables the "comprehensive multidimensional separation" through its trapping, focusing and reinjection of the sample fractions.[117,125,133–135] Figure 1.7 displays a schematic of a comprehensive two-dimensional gas chromatograph instrument with the difference between it and Figure 1.6 being the modulator connected to the second dimension column (indicated by the number 2). As a result, the sample is introduced to the first dimension for separation and after eluting from the first dimension (indicated by the number 1), the eluent enters the modulator to be focused then injected to the second dimension.

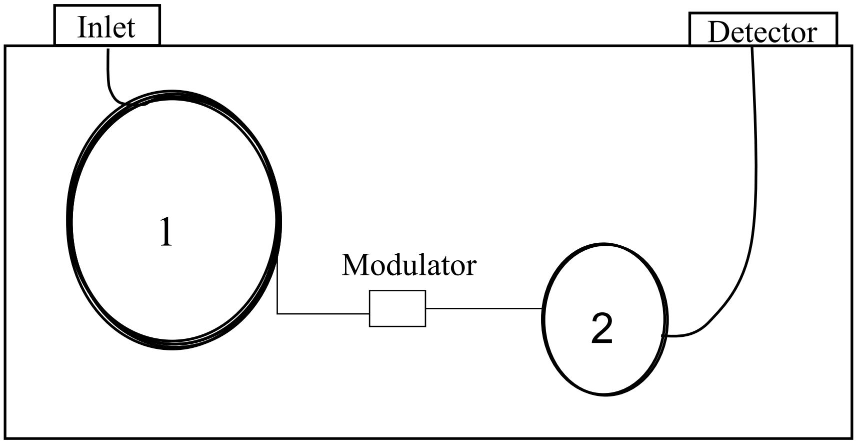


Figure 1.7: General Schematic of a GC×GC Instrument Set up

1.5.1 Modulation

The introduction of the modulator for periodic sampling of the effluent makes GC×GC possible and prevents coelutions or elution order shifts.[117] The first modulator was in Liu and Phillips work which used thermal modulation to create a "true two dimensional gas chromatogram".[130] The modulator injects the individual fractions to allow further separation while maintaining the primary separation.[14,117,136] Two types of modulation are thermal modulation which operates on the basis of temperature, and flow modulation which operates with two independent flow rates being coupled together.[14,134,136] Thermal modulation is commonly used as it gives an increase in sensitivity.[125,134,137] One type of thermal modulator uses cryogens and involves a quad jet design consisting of two cold jets for trapping and two hot jets for releasing the analytes.[135] Drawbacks of thermal modulation include breakthrough of high volatility compounds and higher cost of analysis from usage of cryogens.[14,134,137] Flow modulation has grown in use and example designs are the Agilent Technologies' Capillary Flow Technology (CFT) and the INSIGHT modulator from SepSolve.[134,137] Flow modulators operate by filling a sample loop with the first dimension effluent and then the loop is flushed with a high flow of auxiliary carrier gas to inject fractions into the second dimension.[136] The high flow rate in the second dimension leads to narrow injection bands and fast separations.[136] It is important to note that the high flow rates are not compatible with mass spectrometers, therefore, the flow is usually split the mass spectrometer and a second detector such as a FID.[136] Flow modulation has the ability to modulate more volatile compounds which makes it appealing for the analysis of airborne VOCs.[134]

1.5.2 Environmental Applications of GC×GC

Environmental samples are quite complex due to the various compounds present in the samples and the fact that analytes of interest are at trace level.[9,22,26,27,117,126] Furthermore, in order to enhance environmental monitoring, GC×GC can be used to go beyond targeted methods and determine other contaminants present through nontargeted analysis.[9,19] One of the earliest examples of GC×GC in environmental analysis is Gaines et al. in their work determining the sources of oil spills in water using a thermally modulated GC×GC.[138] Here it was shown that this instrumentation enabled similar marine diesel fuels to be differentiated due to the different compounds present in the two samples.[138] A couple years later, Beens et al. showcased that this technique could be used in surface water analysis and they explained the benefit of having two retention times for identification.[139] Beens et al. were able to separate a sample that contained a wide range of compounds including polyaromatic hydrocarbons, halogenated hydrocarbons, chlorinated aromatics, nitrogen containing compounds, aldehydes, alcohols, quinolines, phthalates and pesticides/herbicides via a CO_2 cryogenic modulator.[139] These initial cases of water analysis showed the suitability of GC×GC to separate complex samples in environmental analysis with detection using mass spectrometry.[26]

In 2000, Lewis et al. applied GC×GC to ambient air monitoring for VOCs in urban air samples due to VOCs' environmental impact and the comprehensive separation revealed hundreds of compounds.[140] This was a significant increase over the 20 – 30 peaks observed in the one dimensional GC separation, many of these coeluted with each other in the one dimensional separation.[140] Hamilton and Lewis later looked at both fast GC-TOFMS and GC×GC-FID for both gasoline and urban air samples.[23] Key highlights from this work are the increased resolution and the peak enhancement which enables lower concentrations of analytes to be seen.[23] Other analytical methods such as GC-FID, GC-MS and heartcut GC have the issue of many coelutions which mask the presence of monoaromatics.[23] Kallio et al. showcased the analytical abilities through method validation of this technique as well as the nontargeted power of GC×GC for aerosol analysis.[141] The nontarget capabilities of GC×GC can be an important tool in the analysis of complex samples such as in environmental air analysis. Kallio et al.'s analysis of particulates for polyaromatic hydrocarbons using GC×GC displayed an estimated limit of detection of 0.18 ng/m^3 and LOQ of 0.27 ng/m^3 .[141] In another case of aerosol analysis, direct thermal desorption was coupled with GC×GC and with the usage of scripts for classification which can be included in data processing enabling classifying of compound classes.[27] Later Xu et al. employed flow modulation for urban air analysis in Shanghai for straight chain alkanes and polyaromatic hydrocarbons using solvent extraction which gave better resolution for compounds of interest in one analysis.[142] The benefit of flow modulated GC×GC stated in Xu et al.'s 2015 work is the lower cost of analysis while allowing easier monitoring of polluted air.[142] An online application of ambient aerosol monitoring with a thermal desorption aerosol which coupled with GC×GC enabled hourly measurements with greater separation power.[143,144] Several works have coupled GC or GC×GC to TD to analyze ambient air samples for VOCs.[111]

1.6 Overview of Thesis

To improve environmental air monitoring, new methods are needed to replace outdated government methods as these present the risk of missing pollutants. To fill gaps in current methods, comprehensive two-dimensional gas chromatography is an excellent tool to see the different harmful VOCs that can be present in the air. The power of comprehensive two-dimensional gas chromatography to separate complex mixtures has been shown since its development due to the additional degree of separation in this instrumentation. While there has been extensive work using GC×GC in various environmental monitoring applications since its first use, environmental monitoring laboratories continue to use older methods with target lists. The need for hybrid targeted-nontargeted methods presents itself due to the wide range of VOCs with an impact on both human health as well as on the environment itself. Moving to these hybrid methods will aid analytical chemists in the identification of unknown contaminants while still monitoring the known compounds of interest which leads to better enforcement of air quality guidelines. Figure 1.8 shows the schematic of the method presented in this thesis, adapted from Hoh et al's 2009 work.[145] Complex samples such as environmental air samples have the potential to have a large number of compounds, both target compounds and nontarget compounds. The ability to use a single analysis for both quantification of known VOCs of interest and discover other VOCs present in the sample can be extremely beneficial to environmental monitoring laboratories. The ability to do both types of analyses at the same time simplifies the number of methods needed and gives analysts a unique tool. The goal of the method presented in this thesis is to preform both the targeted and nontargeted analysis at the same time to give analysts a powerful tool.

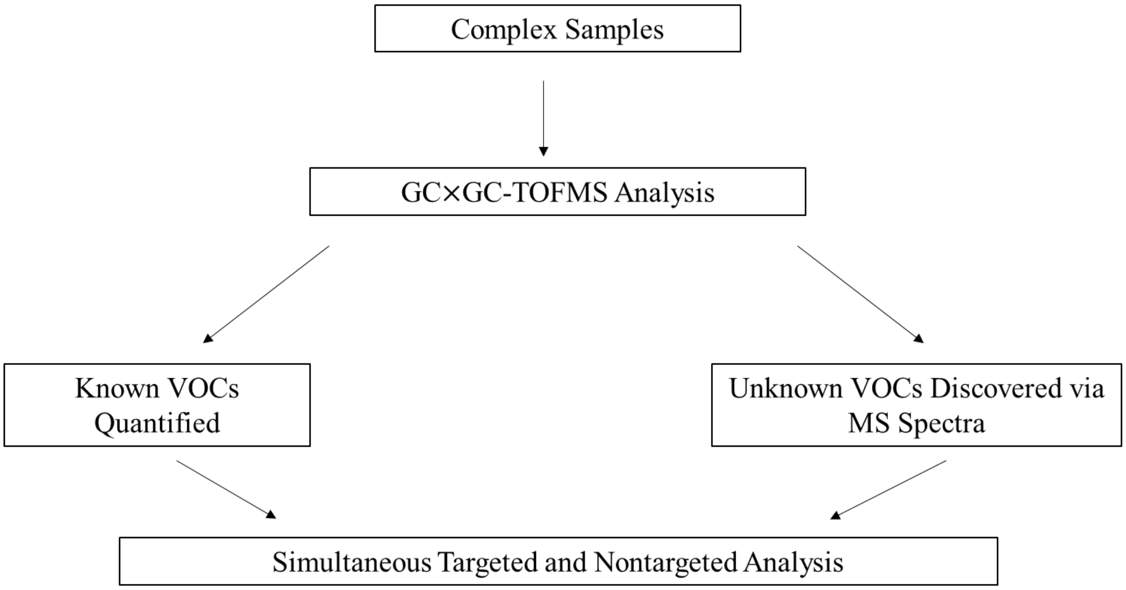


Figure 1.8: Schematic of a Hybrid Targeted-Nontargeted Analytical Method Adapted from Hoh et al.[145]

The hypothesis of this thesis is that environmental air monitoring will benefit from a hybrid targeted-nontargeted method due to its ability to see the full sample profile. The objective of this thesis to present a hybrid targeted-nontargeted TD-GC×GC-TOFMS method for the monitoring of airborne VOCs, then explore applications that this method can cover. Figure 1.9 shows the overall process to be used in this work, starting from sampling, and ending with analysis. The analysis at the end of this process is the hybrid targeted-nontargeted method developed in this thesis which enables the full sample profile to be seen. Chapter 2 will cover the development of an optimized hybrid TD-GC×GC-TOFMS method with attention on desorption parameters after creating the separation method. Chapter 3 of this thesis focuses on different applications of the method developed in Chapter 2, using both indoor and outdoor air sampling. Overall, the objective of this thesis is to update environmental air monitoring methods beyond what is currently being done with current government-published methods. Here coupling thermal desorption to comprehensive two-dimensional gas chromatography – time of flight mass spectrometry enables this hybrid method. Ideally, this method can be implemented in environmental monitoring laboratories to discover new VOCs present in air which expands the range of a single method.

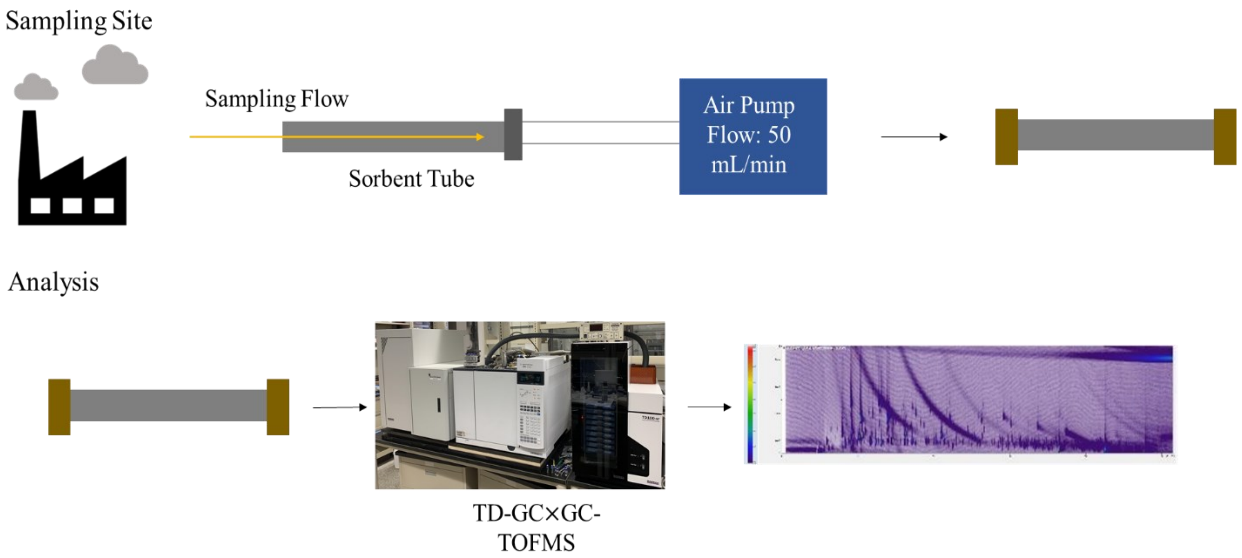


Figure 1.9: Air Sampling and Analysis Process Using TD-GC×GC-TOFMS for Hybrid Targeted-Nontargeted Air Monitoring

Chapter 2 Development of a Hybrid Targeted-Nontargeted TD-GC×GC-TOFMS Method

2.1 Introduction

VOCs are present in the atmosphere as a result of human activities as well as natural occurrences such as wildfires.[1] The number of VOCs of interest is growing due to new compounds entering the environment as well as degradation and reaction products which makes it difficult to get a full view of all of the contaminants present with methods using GC-MS.[83] There are several types of analysis which can be employed in environmental monitoring and one example is targeted analysis. Targeted analyses look for specific compounds and in some cases there are additional steps of sample preparation to remove interferences.[146] The EPA has targeted air monitoring methods such as the TO-15 and TO-17 methods which focus on compounds such as the ones in previously discussed in Chapter 1.[17,18] A disadvantage of targeted methods is that the full range of VOCs present in the sample are not seen and this leads to the usage of another type of analysis, nontargeted analysis.[19] Nontargeted analysis is an important tool that is employed when it is essential to know all the compounds present in a sample.[9,19,145,146] Coupling targeted and nontargeted analyses together creates a more powerful hybrid method as these together enable important unknown compounds to be identified as well as target analyte quantification.[147] VOC monitoring programs would be improved with an addition of a nontargeted component to the method as this presents the ability to detect the presence of new contaminants.[19] Targeted-nontargeted methods enable patterns present in samples to be more easily seen compared to targeted methods relying on target lists alone.[148] GC×GC in combination with time of flight mass spectrometry is ideal for hybrid targeted - nontargeted methods due to the separation power and mass spectral information.[126,145,146] These two techniques combined allows for the discovery of unknown pollutants in complex environmental samples.[83] Therefore, these instruments were employed for the development of the hybrid method for measuring VOCs in the atmosphere.

Sampling and sample preparation are critical in any analysis, therefore, in the case of ambient air sampling it is desirable to collect large volumes and see the full range of VOCs present in the air.[93,107] This is possible through sampling with multisorbent tubes then using thermal desorption to inject the sample for analysis.[74,93,107] Using a sorbent tube with a single sorbent packed inside limits the analyst to a specific range of analytes to be sampled at a single time.[93] A comparison between a single sorbent tube, Tenax TA, and a multisorbent tube, Carbotrap/Carbopack X/Carboxen 569, has shown the multisorbent tube had better performance for the very volatile compounds which provides a deeper analysis of the ambient air.[149] While there may be cases where single sorbent tubes are enough for the desired analysis, when looking for VOCs in ambient air it is recommended to use multisorbent tubes to see a full range of compounds present in the sample.[17,100] Government methods such as the TO-17 method have employed multisorbent tubes as the use of these sorbent tubes have grown.[100] Expansion of the sampling tools to collect a wider range of analytes as in the case of multisorbent tubes, aligns with the goals of a hybrid targeted-nontargeted method via TD-GC×GC-TOFMS.[100,146] Here the main objective of this chapter was to develop the hybrid targeted-nontargeted method as well as examine the method sensitivity using limits of detection and limits of quantification. Another objective was to examine the effect of storage time and temperature on the analyte response. The hypothesis for the work in this chapter was that the developed method would enable low detection limits which would benefit trace analysis and that storage in refrigerated conditions would improve storage times.

2.2 Experimental

2.2.1 Sampling

Air samples were collected using GilAir-3 sampling pumps (Sensidyne, St. Petersburg, FL, USA) which were calibrated using Gilibrator 2 Calibrator (Sensidyne, St. Petersburg, FL, USA) to set the sampling flow rate. Stainless steel sorbent with the following dimensions were used: 89 mm × 6.4 mm × 5 mm which had 6 cm of sorbent packed inside.[90] Sorbent tubes used for sampling were purchased from Markes International (Markes International Ltd., UK) and Camsco (Houston, TX). These sorbent tubes had three sorbents packed inside packed from weakest sorbent to strongest sorbent, Tenax TA/ Carbograph 1/Carboxen 1003 (or Tenax TA/ Carbograph 1/ Carbosieve SIII). Prior to reaching the sampling site, the sampling pumps were calibrated to a flow rate between 49-51 mL/min based on the literature value for the optimal sampling flow rate of 50 mL/min.[90,103] Sample time was 60 min based on EPA sampling parameters and the start time as well as the end time was recorded.[17]

2.2.2 Standards and Solvents

Standards were purchased from Absolute Standards (Hamden, CT, USA) and the EPA Method 524.2 Volatiles standard mixture was used for method development. The calibration range used was 0.49 – 18.75 mg/L in ACS grade methanol (99.8% assay). Sorbent tubes, Tenax TA/ Carbograph 1/ Carboxen 1003 (or Tenax TA/ Carbograph 1/ Carbosieve SIII), were loaded with standard solutions in the sampling direction which was indicated by the arrow on the tube. Microman (Gilson Incorporated, WI, USA) positive displacement pipettes were used to dispense standard solutions during preparation. The mass of each volume of solution added was recorded and the density of methanol at the current temperature were used to determine the actual concentration of each standard. When loading the standards onto the sorbent tubes for desorption, calibration and storage experiments, a Hamilton 10 µL syringe was used to apply 1.0 µL of standard to the sampling end of the sorbent tube. The volume was recorded before and after loading solutions on the sorbent tubes to determine the volume added. Figure 2.1 demonstrates how standards were loaded onto sorbent tubes. The final volume was subtracted from the initial volume in order determine the actual volume spiked on the sorbent tube. The actual volume was recorded to account for any differences in volume added to the sorbent tube. The EPA TO-17 method states that the syringes can be used to load standards on to sorbent tubes if a GC inlet could not be used to pass carrier gas through the sorbent tube while loading the standards.[17] In the EPA method, the authors state that the standards should be loaded on the non-sampling end but this would not work for multisorbent tubes.[17] Here loading the standards in the sampling direction works for multisorbent tubes as there is no risk of VOCs being trapped on strong sorbents. There is the risk of VOCs being lost using this methods as the standards do not quite reach the proper sorbents and more volatile VOCs may be lost when loading.

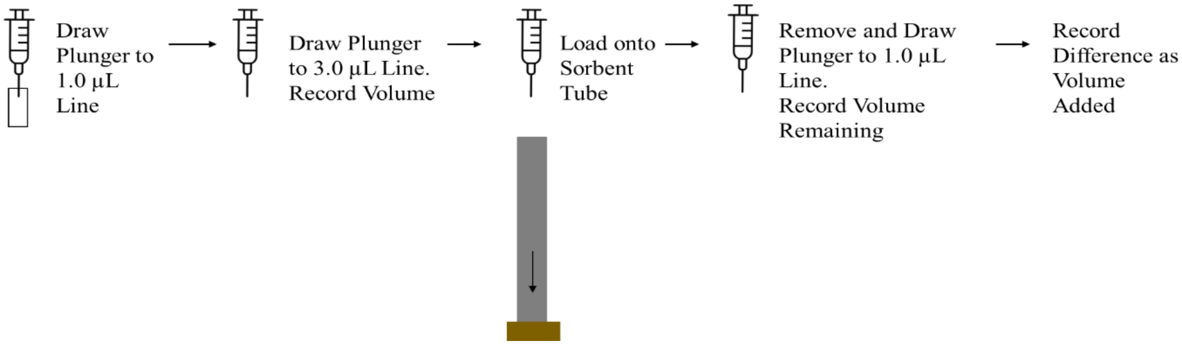


Figure 2.1: Procedure for Loading Standards onto the Sorbent Tubes for Analysis using a Hamilton Syringe

2.2.3 TD-GC×GC-TOFMS/FID Conditions

Samples were thermally desorbed in an automated TD unit (TD 100-xr Markes International Ltd., UK) then analyzed in the GC×GC system, an Agilent Technologies 7890A GC. Liquid standards for separation optimization were injected in volumes of 1 µL using an Agilent Technologies 7683 Series Injector. Grade 5.0 helium carrier gas (Linde Canada Inc., Mississauga, ON, CA) was used for both the GC×GC analysis and the TD process. The first-dimension column was a 30 m × 0.25 mm; 1.0 µm df Rtx-5, 5% phenyl phase column, with the second-dimension column being a 5 m × 0.25 mm; 0.5 µm df Rtx-200, trifluoropropylmethyl polysiloxane column. A 2.5 m × 0.100 mm fused silica bleed line was used to provide an outlet for the carrier gas if the sample loop is over filled and allow for reversed flow for flushing the sample loop.[136] Liquid injections were performed for optimization of the separation and the inlet was held at 250 °C and split ratio of 20:1 split. Initial oven temperature was set to 30 °C then the temperature was ramped at rate 5 °C/min, optimal heating rate, to a final temperature of 250 °C. The initial temperature was held for four minutes while the final temperature was held for five minutes. Flow rate for the first-dimension column was set to 1 mL/min while the second-dimension flow rate set to 20 mL/min. The modulator used here was the SepSolve INSIGHT reversed fill/flush modulator (SepSolve Analytical Ltd., Peterborough, UK). The modulation period was set to 2.0 s with a fill time of 1.9 s and a flush time of 0.1 s. Figure 2.2 shows a schematic of the SepSolve INSIGHT modulator used in this work and how the columns are connected, adapted from the SepSolve guide.[150] The sample undergoes separation in the first dimension before entering the sample loop where it is focused than injected into the second dimension.

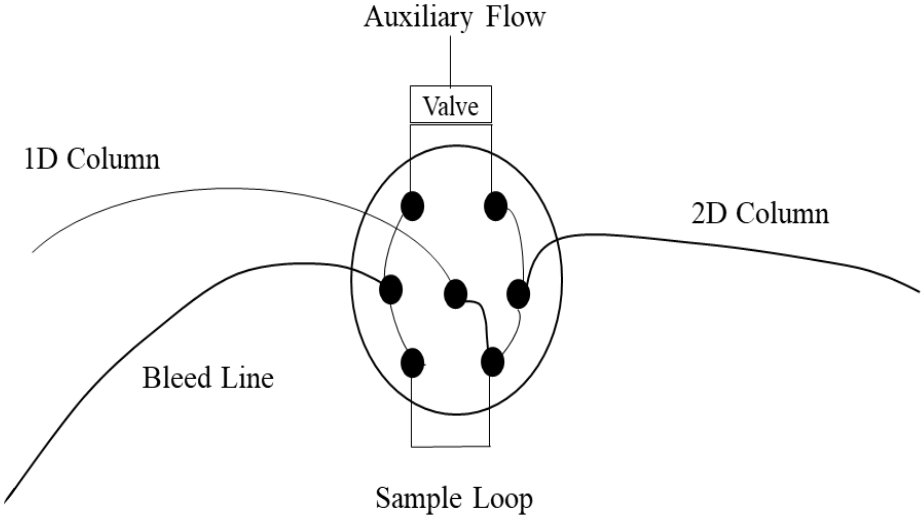


Figure 2.2: Schematic of the SepSolve Insight Modulator used in this Thesis[150]

For the thermal desorption conditions, purge time was set to 0.0 minutes to prevent analyte loss before desorption then the sorbent tube was desorbed in the tube oven at 250 °C for ten minutes at a flow rate of 50 mL/min. The focusing trap (General Purpose Carbon) was initially held at - 25 °C then heated to 300 °C and held there for three minutes for the injection with a split flow of 20 mL/min. The thermal desorption unit flow path temperature was set to 150 °C. The second-dimension flow was split between the FID and the Markes BenchTOF-Select (Markes International Ltd., UK) with a ratio of 3.3:1. Figure 2.3 shows an adapted schematic of the splitter which sends a larger amount to the FID and a reduced flow to the mass spectrometer.[150] The splitter is needed due to the high flow rate in the second dimension which is too high to be used with a mass spectrometer.[136] The Markes BenchTOF was set to collect at an acquisition rate of 100 Hz and collected from 40 – 300 m/z. The transfer line temperature was set to 250 °C and the ion source temperature was set to 250 °C. Tandem ionization was employed for this analysis with the two ionizations energies being 70 eV and 12 eV. The filament voltage was set to1.7 V and for liquid injections, the filament delay was set to 460 s. FID temperature was 300 °C with a helium makeup flow of 20 mL/min, air flow of 250 mL/min and hydrogen flow of

80 mL/min. The TD-GC×GC-TOFMS/FID system was controlled using ChromSpace software version 1.5.1 (SepSolve Analytical Ltd., Peterborough, UK).

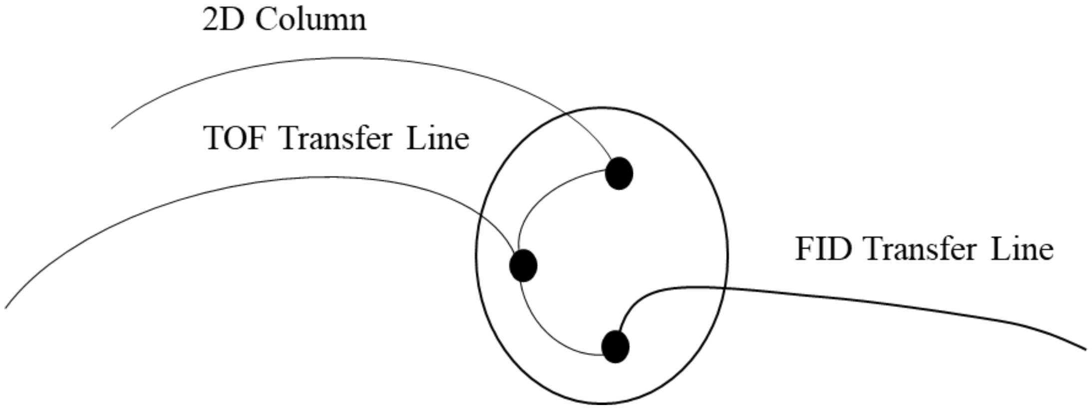


Figure 2.3: Setup of the SepSolve Splitter used in the Instrument[150]

Table 2.1 has a summarized list of the optimized instrumental conditions used in this thesis unless otherwise stated. Experiments in Section 2.3 Results and Discussion were used to determine conditions for the thermal desorption process and GC×GC parameters.

Table 2.1 Optimized Method Conditions Used in This Thesis

Thermal Desorption	
Desorption Time (min)	10
Desorption Temperature (℃)	250
Desorption Flow Rate (mL/min)	50
Focusing Trap Split Flow (mL/min)	20
Trap Initial Temperature (℃)	-25
Trap Final Temperature (℃)	300
Final Temperature Hold (min)	3
Flow Path Temperature (℃)	150

Liquid Injection	
Inlet Temperature (°C)	250
Trap Split Ratio	20:1
GC×GC Conditions	
First Dimension Column	Rtx-5, 5% phenyl phase
First Dimension Column	30 m×0.25 mm; 1.0 µm df
Second Dimension Column	Rtx-200, trifluoropropylmethyl polysiloxane
Second Dimension Column	5 m×0.25 mm; 0.5 µm df
Bleed Line	2.5 m×0.100 mm
Initial Temperature (°C)	30
Initial Hold (min)	4
Temperature Ramp (°C/min)	5
Final Temperature (°C)	250
Final Temperature Hold (min)	5
First Dimension Flow (mL/min)	1
Second Dimension Flow (mL/min)	20
Modulation Period (s)	2.0
Fill Time (s)	1.9
Flush Time (s)	0.1
BenchTOF Select Conditions	
Solvent Delay (s)	460
Transfer Line Temperature (°C)	250
Ion Source Temperature (°C)	250
Mass Range	40-300 m/z
Data Acquisition Rate (Hz)	100
Ionization Energy 1 (eV)	70
Ionization Energy 2 (eV)	12
Filament Voltage (V)	1.7

FID Conditions	
Temperature (℃)	300
Air Flow (mL/min)	250
Hydrogen Flow (mL/min)	80
Helium Makeup Flow (mL/min)	20

Figure 2.4 shows the instruments used in this thesis in both research chapters and this contains the Agilent 7890A GC, which was set up for GC×GC, the Markes TD 100-xr and the Markes BenchTOF Select. Also seen in Figure 2.4 is the Agilent Technologies 7683 Series Injector used for liquid injections into the system for calibration work. The TD 100-xr thermally desorbs the sample to be separated on the GC×GC system and the Markes BenchTOF Select allows for compound identification through mass spectral library searching. This mass spectrometer allows for two ionization energies to be used; however, the 70 eV results were the only ones used in this work.

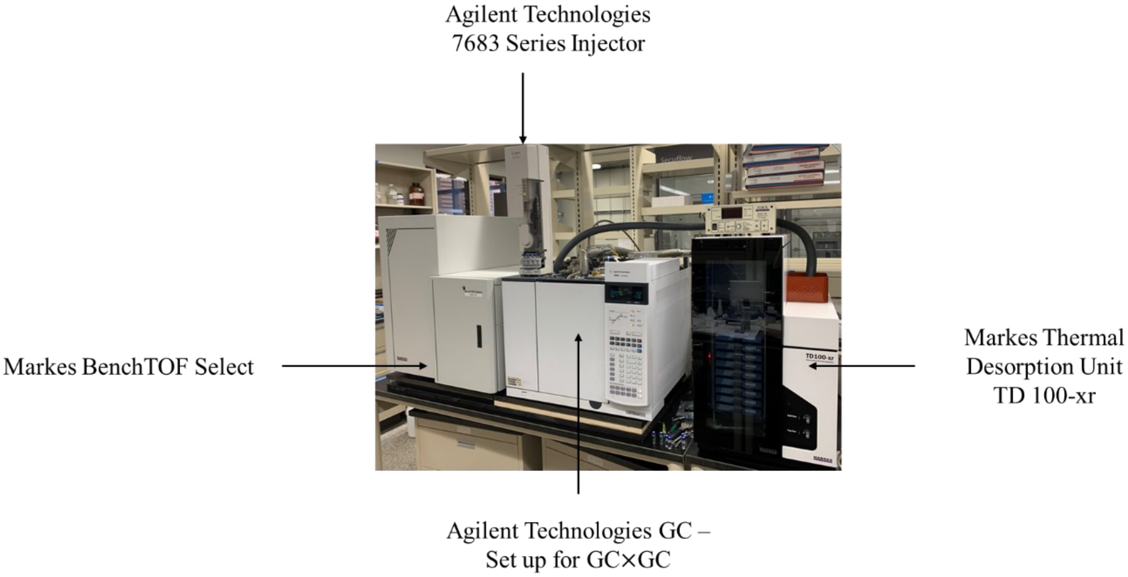


Figure 2.4: TD-GC×GC-TOF/FID Instrumental System Used in This Thesis for the Analysis of VOCs

2.2.4 Data Processing

Data processing took place using ChromSpace software version 1.5.1 (SepSolve Analytical Ltd., Peterborough, UK) using the curve fitting peak detection algorithm with three points used for smoothing. Baseline during processing was set to natural and stencils were used for processing standards of interest. NIST and Wiley mass spectral databases were used for library searching for the identification of compounds. Integration parameters for the overall chromatogram were minimum area, which is the lowest peak area to be detected, minimum height, which is the lowest peak height to be detected, and the smallest peak width was set using minimum peak width. The minimum area was set to 10000, minimum height was 10000 and minimum width of 0.0100. Parameters for detecting the target compounds were minimum area of 1000, minimum height of 100 and minimum width of 0.0100. Identification parameters were the same as the integration parameters for peak detection and in addition to those the method used three qualifier ions and the uncertainty was set to 50 %. The quantification ions were set for each analyte of interest. Table 2.2 gives a summarized list of the data processing parameters used processing data in this thesis unless otherwise stated.

Table 2.2 List of Data Processing Conditions Used in This Thesis

Integration Conditions	
Overall	
Minimum Area	10000
Minimum Height	10000
Minimum Width	0.0100
Target	
Minimum Area	1000
Minimum Height	100
Minimum Width	0.0100
Identification Conditions	
Overall	
Minimum Area	10000

Minimum Height	10000
Minimum Width	0.0100
Target	
Minimum Area	1000
Minimum Height	100
Minimum Width	0.0100
Qualifier Ions	3
Uncertainty	50%

2.3 Results and Discussion

2.3.1 Separation Optimization via Liquid Injections

Liquid injections were used to optimize the separation conditions prior to thermal desorption optimization. Column dimensions were selected to allow for increased separation of the volatile analytes, this was done through the usage of thick stationary phase films. Temperature programmed conditions were determined with optimal heating rate, OHR = $10°\mathrm{C}/t_m$, which was used for the ramp rate. The initial temperature was set to 30 ℃ to hold the more volatile compounds and allow adequate separation of these with initial hold set to be longer than the planned focusing trap conditions, four minutes. Final temperature was determined based on the elution of the least volatile compounds in the standard mixture with a hold to allow for potential semi-volatile organic compounds in future samples. First- and second-dimension flow rates were determined using conditions recommended by SepSolve experts. The parameter last optimized was the modulation period and experiments used to compare a 4.0 s modulation period to a modulation period of 2.0 s. The longer modulation period was selected in case of wraparound of analyte peaks in the chromatogram and the shorter modulation period was selected to compare resolution of compounds. A 1.0 µL injection of a 50 mg/L standard mixture of EPA VOCs was performed using each method with the only difference between the two methods being the modulation period.

Figure 2.5 shows the separation along the entire chromatogram using the 4.0 s modulation period while Figure 2.6 shows the separation over the entire chromatogram using the 2.0 s modulation period. The second-dimension separation resolution is comparable in both figures therefore the main considerations for the determination of the modulation period is the extent of wraparound and first dimension resolution. While the 4.0 s modulation period does allow for decreased wraparound due to the greater time for filling the sampling loop, the analytes showed decreased resolution in the first-dimension separation. In comparison, the 2.0 s modulation period allows for better resolution in the first dimension due to less coelutions which is significant for both identification and quantification.

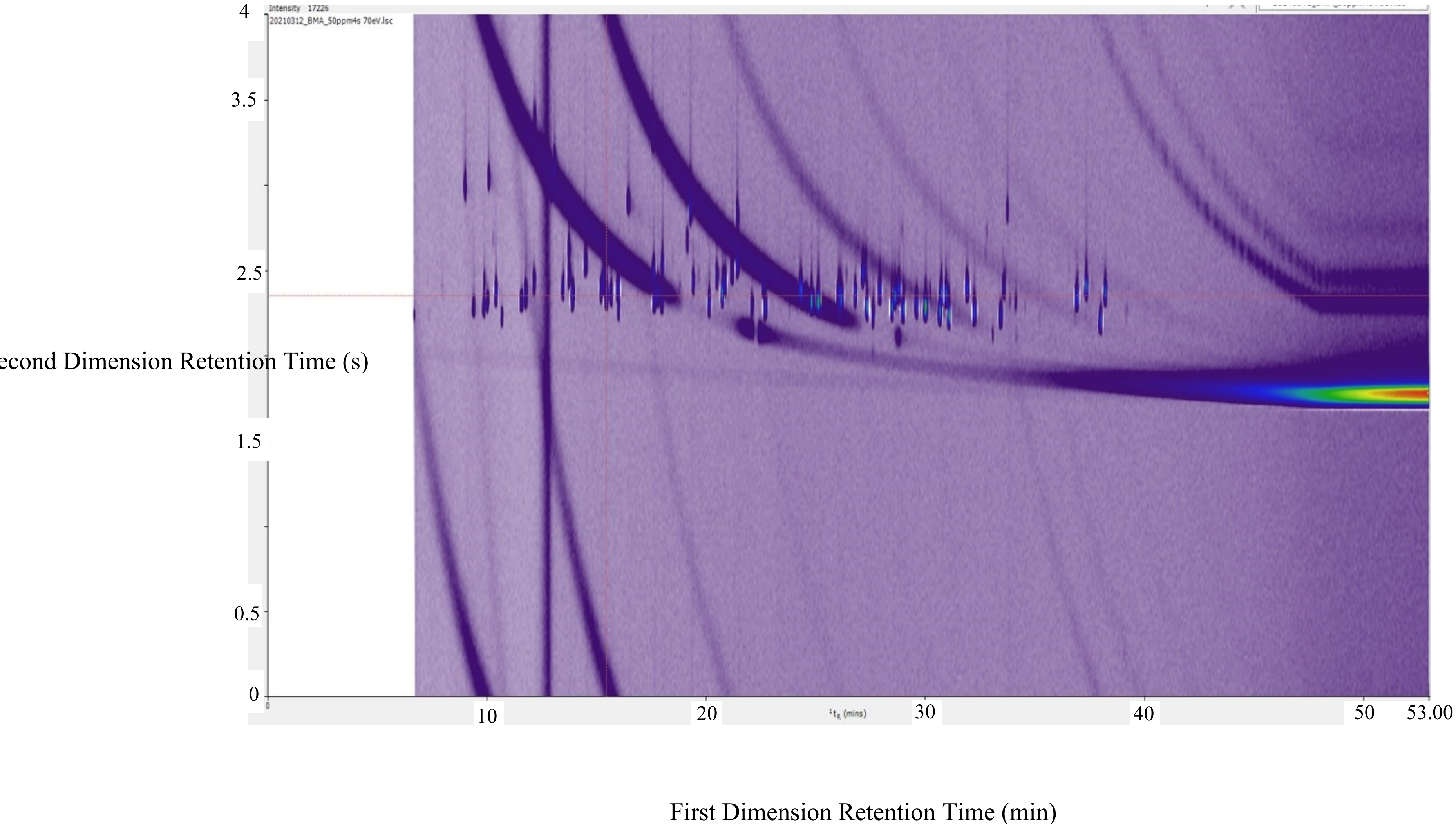


Figure 2.5: GC×GC Chromatogram of a 1.0 µL Injection of an EPA Standard Mix Using 4.0 s Modulation Period

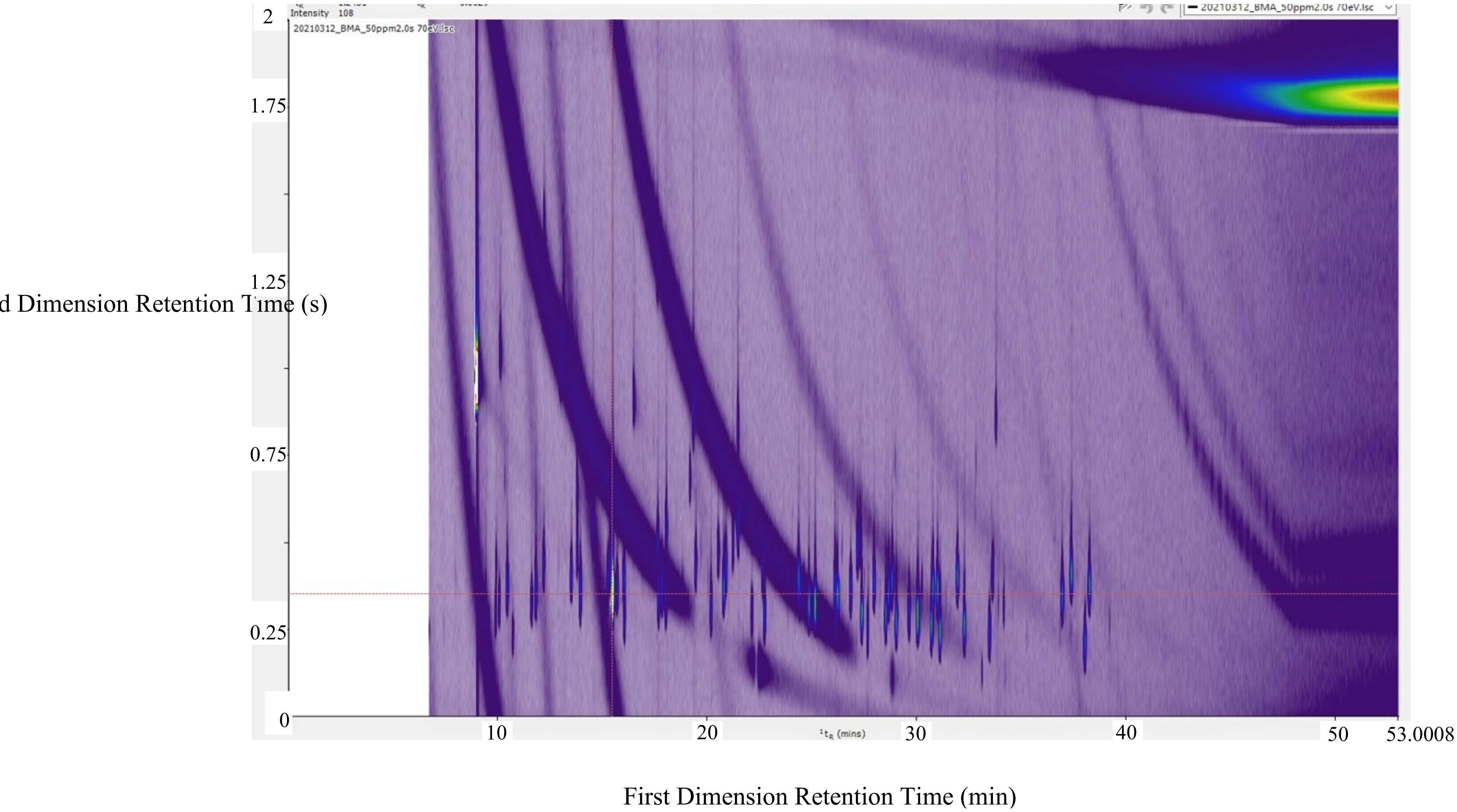


Figure 2.6: GC×GC Chromatogram of a 1.0 μL Injection an EPA
Standard Mix Using 2.0 s Modulation Period

At first glance, the first-dimension resolution appears to be comparable in both methods. However, upon closer inspection of the resolution in both separations, the differences between the two methods can made more apparent. Figure 2.7 compares the separation in both methods by looking specifically at three compounds: trichloroethylene (1), dibromomethane (2), and bromodichloromethane (3). Visually, the peaks appear to have similar resolution in both methods, however when the resolution is calculated, using $Rs = \frac{t_{r2}-t_{r1}}{w_{avg}}$, between the analytes the difference between the two methods can be seen. In the case of trichloroethylene and dibromomethane, the first-dimension resolution in the 4.0 s modulation period method was calculated to be 0.67 while with in the 2.0 s modulation period, the resolution increases to 0.81. The same trend can be seen with dibromomethane and bromodichloromethane as the 4.0 s modulation period was determined to have a resolution of 0.61 while the resolution in the 2.0 s modulation period method was increased to 0.96.

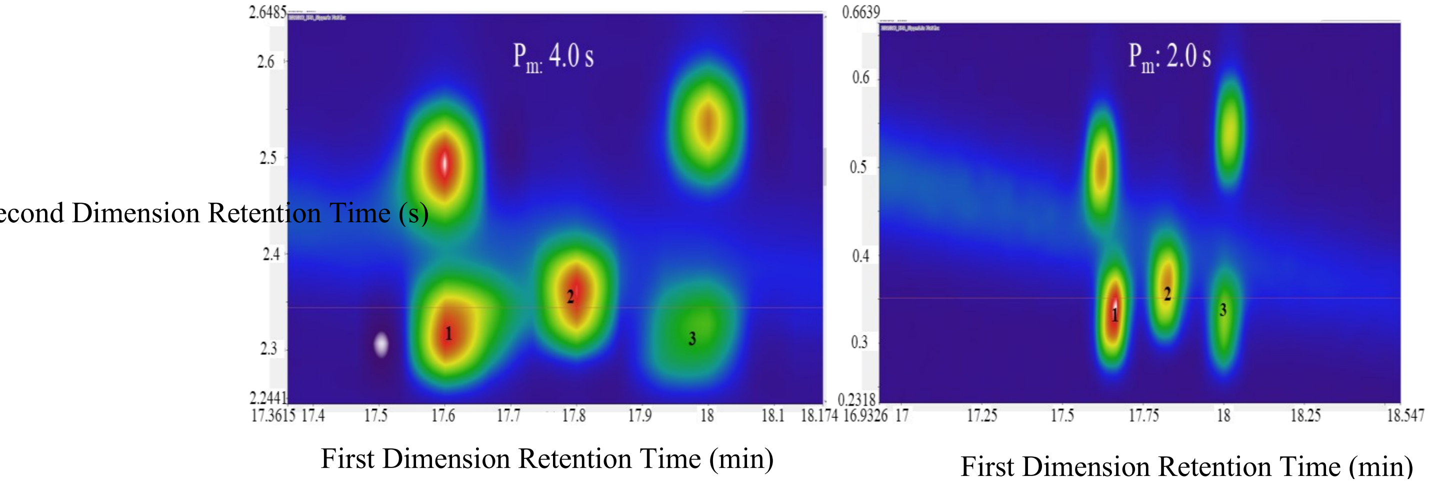


Figure 2.7: Close up on GC×GC Chromatograms of 4.0 s and 2.0 s Modulation Periods for Comparison of Resolution

The resolutions mentioned previously and shown in Figure 2.7 shows the improvement in resolution seen in the 2.0 s modulation period over the 4.0 s modulation period. There are cases where compounds are closer than the ones in Figure 2.7 therefore if the loss of resolution in 4.0 s method is significant enough then two compounds can completely coelute with a neighboring compound causing issues with identification and quantification. Figure 2.8 shows styrene (1) and o-xylene (2) in both separations with these compounds showing this issue perfectly. On the left is the 4.0 s separation and here the styrene peak is coeluting with the o-xylene peak. In that separation the data processing could not detect styrene and it was missed in the peak table which would result in it being missed without intervention from a user. In these cases, the identity of the coeluted compound may only be found by clicking on the peak in the chromatogram in the software. The need for user intervention may slow the data processing and analysis process. On the right side of Figure 2.8, the 2.0 s separation shows two distinct peaks for both styrene and o-xylene. Furthermore, the data processing software was easily able to detect both compounds and as a result neither compound was missed in the peak table thus two distinct responses for both can be seen. While in cases where the area of one compound is combined with another it is possible to determine its presence, the more automated the process is the easier it will be for the analyst to give results. Better quality peak reports will allow for data to be processed and analyzed with little analyst intervention which may lower the time needed to analyze the data.

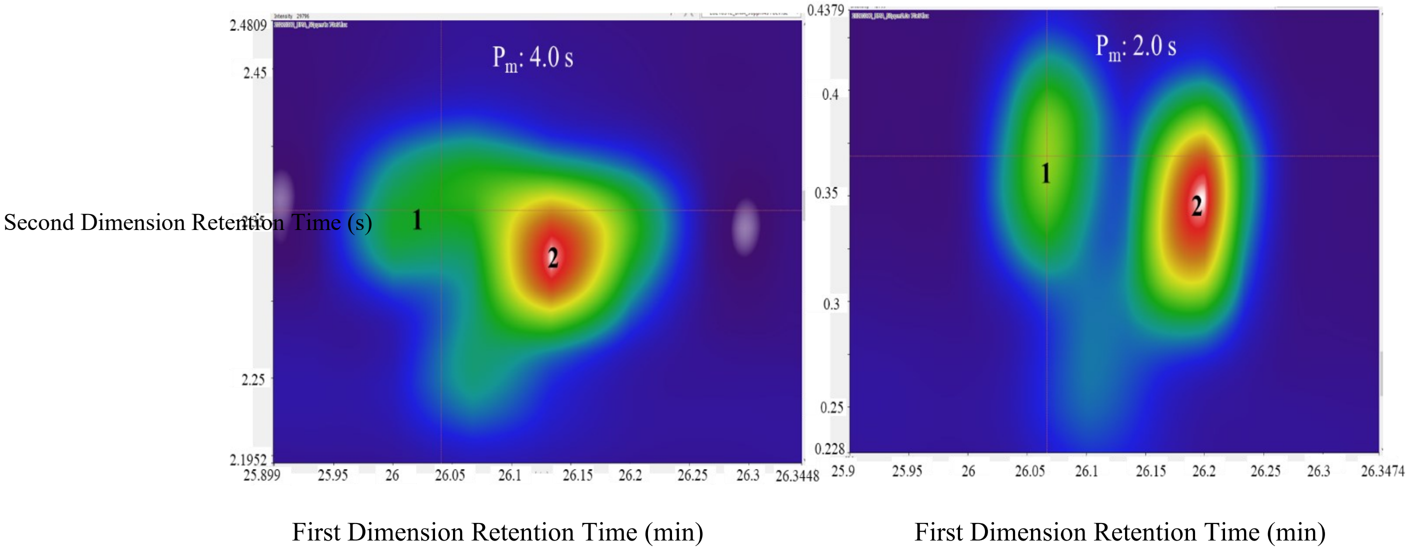


Figure 2.8: Close up on GC×GC Chromatograms of 4.0 s and 2.0 s Modulation Period for the Comparison of Resolution of Styrene (1) and o-Xylene (2)

After examining the resolutions of compounds in both separations, the optimal modulation period for the analysis of VOCs was determined to be 2.0 s to prevent loss of resolution. There was no significant wraparound in the 2.0 s separation, thus the main factor for determining the optimal modulation period was the difference in the first-dimension resolution.

This increased resolution aides not only the detection of the target analytes used in the optimization process but also the detection of unknown compounds. The phenomenon seen here can be explained by looking at the sampling rate of the system. Here the larger modulation period causes the first dimension effluent to be undersampled.[151] This low sampling rate impacts the separation which leads to the loss of resolution seen in Figures 2.7 and 2.8. In order to prevent peaks recombining in the second dimension separation, peaks exiting the first dimension need to be sampled a minimum of three times.[151] A term used to further examine this issue is the modulation ratio which relates the peak width to the modulation period and gives the sampling rate.[152] Larger modulation ratios gives increased sampling of the peaks from the first dimension which enable the preservation of the first dimension separation.[152] With the optimization of the modulation period finished the GC×GC method optimization was complete and the next step in the process was to move to the thermal desorption part of the method.

2.3.2 Optimization of Thermal Desorption Method

2.3.2.1 Optimization of Desorption Conditions

The goal for optimization of the thermal desorption conditions is to achieve complete desorption of the analytes on the sorbent tube. Complete desorption is essential for obtaining accurate results for reporting which is critical for an air monitoring laboratory. To ensure complete desorption, experiments were done to check the desorption at both stages starting with the focusing trap desorption then moving to the sorbent tube desorption. The following analytical sequence was used for these desorption experiments: a sorbent tube loaded with standard was desorbed first, the next run was blank run of the focusing trap which was followed by a second desorption of the sorbent tube. This sequence order is used as sorbent tube desorption involves both stages of desorption which would make it difficult to determine which stage the carryover is from. Therefore, the focusing trap is checked first as it separates the second stage and allows each stage of desorption to be tested.

The desorption experiments started with spiking 1 μL of standard onto the sorbent tubes, beginning with 0.24 ng on column before moving to 0.88 ng on column and finally to the highest standard tested which was 5.6 ng on column. Additional desorption checks were performed on a couple field samples before the final optimized conditions were set. The optimization process began by using desorption conditions recommended by Markes International with a desorption time of five minutes, desorption temperature of 250 ℃, desorption flow of 50 mL/min, focusing trap low of 25 ℃, focusing trap desorption temperature of 300 ℃, and a trap desorption time of three minutes.[153] Focusing trap split flow was set to 10 mL/min giving a split ratio of 10:1 during focusing trap desorption.[153] The following section will expand on the optimization of the split flow rate. Universal sorbent tubes were used for the optimization process as well as future sampling.

Looking first at the focusing trap desorption condition, the Markes recommended conditions were able to facilitate complete desorption of the focusing trap. The condition that needed to be optimized was the desorption time with the desorption time for complete desorption determined to the be ten minutes. Figure 2.9 compares the initial run of the 5.6 ng on column standard (top) to the following focusing trap blank (bottom). The chromatograms shown are focused particlarily on the baseline in order to see if there were any traces left in the focusing trap desorption and there were no peaks seen in this run. The fact that there were no peaks present in the focusing trap blank following an intial run of the 5.6 ng on column standard indicates that there is complete desorption under these conditions. Following these experiments, the conditions for the complete desorption of the sorbent tube were examined.

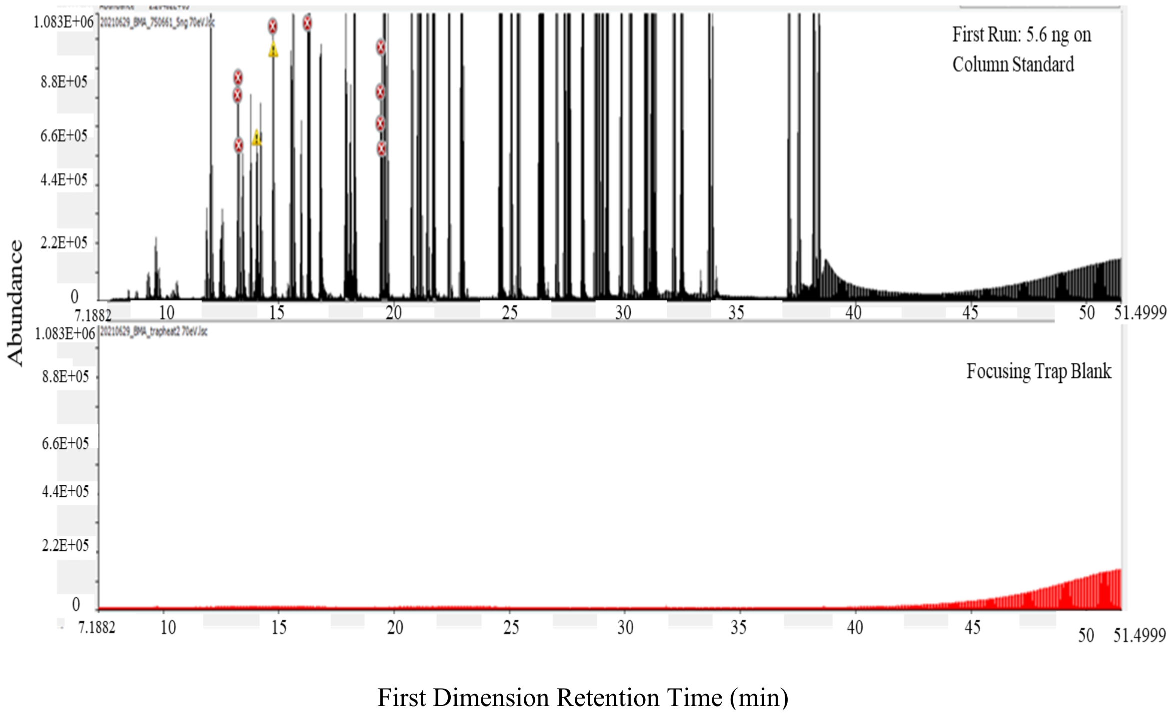


Figure 2. 9: Examination of Focusing Trap Desorption with 5.6 ng of Standard on Column Standard via Comparison of an Initial Run of a Spiked Sorbent Tube (Top Chromatogram) and Focusing Trap Blank (Bottom Chromatogram)

Conditions for the desorption of the sorbent tubes showed the need for increased optimization as the complete desorption was not observed with the initial conditions. Many analyte peaks were seen in the chromatograms of the sorbent tube's second desorption with the initial conditions. Figure A1 in the Appendix shows the profile of the second desorption of the sorbent tube and while there are always artifacts present in sorbents, many of the peaks are traced back to the analytes.[93] Benzene and toluene are two artifacts that were found in the sample and this has been seen in literature, therefore, there was always traces of these compounds due to sorbent use.[154] The extent of desorption with the initial conditions are in Table 2.3 which gives the calculated desorption efficiencies of analytes from the first run of the sorbent tube. While some of the compounds were not seen in the second run or had a desorption efficiency of 99 %, several had desorption efficiencies of 92 % or lower. As there were compounds which did not have at least 99 % desorption efficiency, additional experiments were performed to obtain complete desorption. Using a desorption temperature below the maximum temperature, such as 250 °C, increases the lifetime of the sorbent.[155] Thus to increase the desorption efficiency of the method, the desorption time was increased to allow more time for diffusion to occur. These experiments involved increasing the desorption time to eight minutes and ten minutes then desorbing the sorbent tube a second time to examine the profile of analytes.

Table 2.3: Calculated Desorption Efficiencies at the Initial 5 min Desorption Time

Compound	Calculated Desorption Efficiency
Tetrahydrofuran	98 %
Tetrachloroethylene	91.1 %
Hexachlorobutadiene	99 %
1,3-dichloropropane	92 %
Naphthalene	90 %
Acetone	80 %

Examination of the second desorption of the spiked sorbent tubes with a desorption time of 8 minutes showed complete desorption for all the standard levels tested. Figure A2 in the Appendix shows the impact of increasing the desorption time to 8 minutes with desorption of a 0.24 ng on column standard. This can be further seen in Figure 2.10 which displays this improvement of the desorption conditions with the highest standard spiked onto the sorbent tubes. Peaks present in the second desorption of the sorbent tube are primarily from artifacts rather than the analytes. The close-up view on the baseline in Figure 2.10 shows this particularly well as peaks in the profile of the second desorption have low responses and are few peaks present. Here complete desorption is seen with up to 5.6 ng on column however the ultimate goal is to apply this method to real air samples.

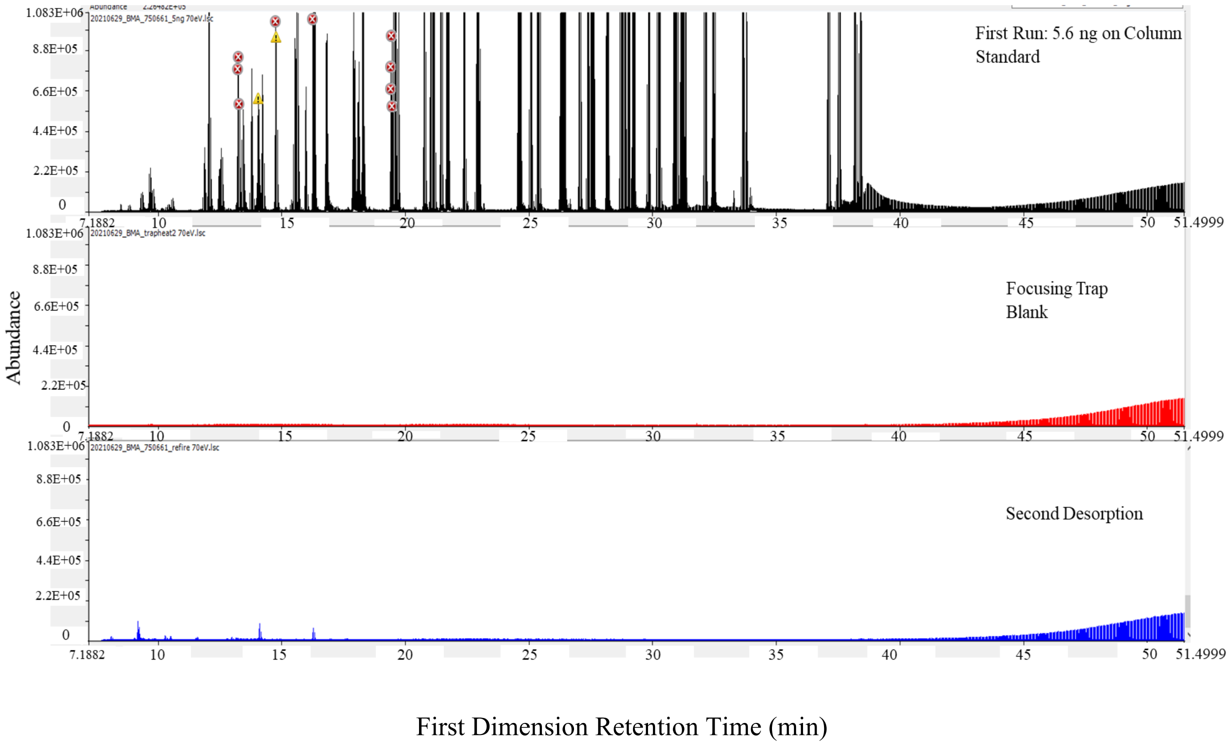


Figure 2.10: Chromatograms Comparing the Initial Run of a Sorbent Tube Spiked by a 5.6 ng on Column Standard (Top), Focusing Trap Blank (Middle) and Second Desorption of the Sorbent Tube (Bottom) for a Desorption Check for Both Stages

Samples collected in the field can have various levels of mass absorbed and it was important to check the desorption to verify that the conditions enabled complete desorption of real samples as well as standards One-hour air samples of the Harynuk Lab space were used for the desorption experiments and the parameters used to completely desorb the standards from the sorbent was not enough to desorb real samples. Figure A3 in the Appendix shows the analysis of the first run with the conditions determined previously which shows several compounds present in the second desorption of the sorbent tube. It is possible to see higher concentrations in real samples which could result in the sorbent tube not being completely desorbed. Another desorption experiment was performed by increasing the desorption time to 10 minutes while maintaining the other conditions. Figure 2.11 shows the results of the final desorption optimization experiment comparing the initial run of a lab air sample to the second desorption. Here focus was placed on the sorbent tube desorption and the profile of the second desorption shows the analytes essentially completely desorbed from the sorbent tube after being heated at

250 °C for ten minutes under a 50 mL/min flow of helium carrier gas. These conditions for complete desorption were then applied to other field samples to determine the presence of both target compounds as well as other VOCs which might be present. The thermal desorption method was determined to enable complete desorption and the final parameter to optimize was the split flow in the focusing trap.

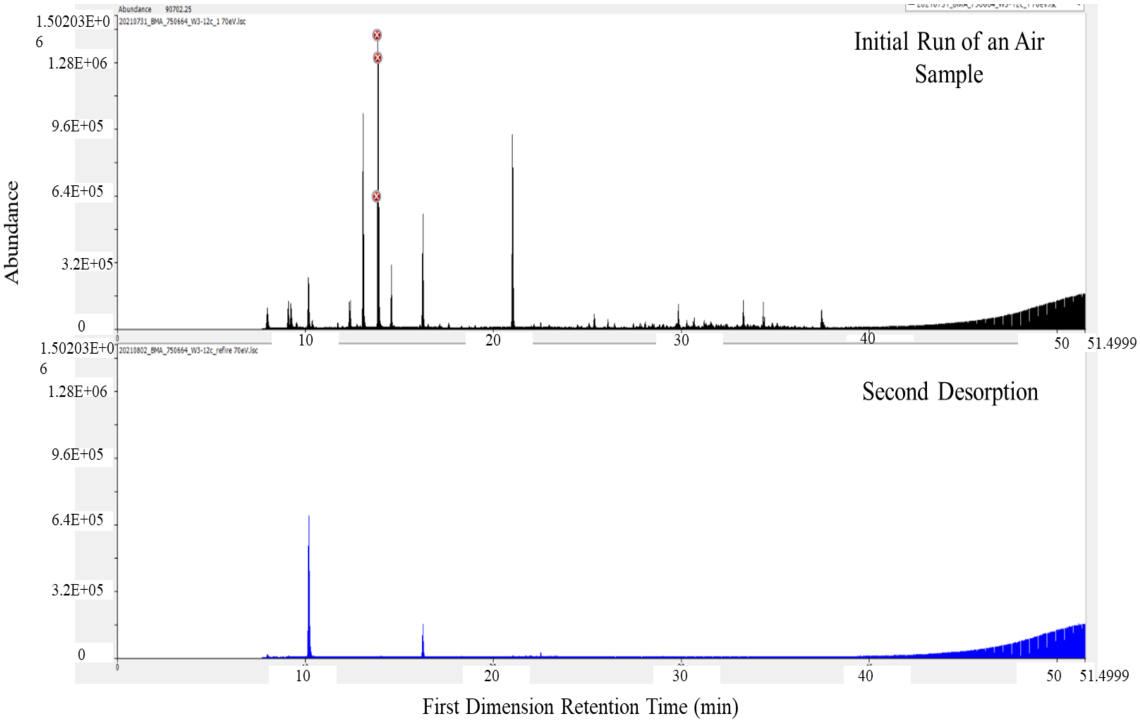


Figure 2.11: Final Desorption Optimization Experiment with Lab Air Sample with a 10 min Desorption Time: Initial Run (Top Chromatogram) and Second Desorption (Bottom Chromatogram)

Following the completion of the experimental work for this thesis, a leak was discovered in thermal desorption unit which had impacted results from several experiments. It is possible that it could have affected optimization of the thermal desorption conditions if significant loss occurred during these experiments. However, the conditions determined in this section were determined to give complete desorption, therefore, they were used for the rest of the thesis.

2.3.2.2 Optimization of Split Flow Conditions

The next stage of optimization involved determining the optimal split flow rate for the analysis. The design of the Markes thermal desorption unit allows for splitting at both stages of desorption depending on the goal of the analysis. For the goal of analyzing trace level VOCs in the air, a split was only used during the second stage of desorption. Here the split flow was used to increase the total flow of gas through the focusing trap which allows for increased desorption. This is recommended by Markes International in cases where the column flow rate is less than 1.5 mL/min.[102] While the flow could be increased, this creates a risk of damage to the thermal desorption unit due to the high pressure. The starting split ratio was set to 10:1 via setting the split flow to 10 mL/min and first dimension column flow of 1 mL/min with the only difference from the Markes International method being the column flow. Two 60 min outdoor air samples were collected at a flow rate between 50-51 mL/min which gave about 3 L of sample collected on the sorbent tube. These samples were then analyzed using the optimized desorption conditions and the split ratio recommended by Markes International. Following these samples, the split flow was increased to 20 mL/min to increase the total flow through the focusing trap for better desorption for real samples.

2.3.3 Calibration of Target List VOCs

2.3.3.1 Calibration and Validation of Target Compounds

Calibration curves were constructed using the seven levels of standards in methanol which ranged in concentration between 0.49 – 18.8 mg/L which gave 0.023 ng on column – 0.89 ng on-column with the 20:1 split ratio. Each of the seven standards was analyzed in triplicate and the analysis order was randomized. Calibration curves were generated from analysis of both liquid injections and thermal desorption of spiked sorbent tubes. The compounds in the standard mixture are VOCs of interest from the EPA TO-17 target list due to the health and environmental risks they pose. These standards were prepared as mentioned in Section 2.2.2 and in the case of thermal desorption calibration, standards were spiked onto the sampling direction of the Universal sorbent tubes using a 10 µL syringe to add 1 µL. The column set for the calibration procedure was a 30 m × 0.25 mm; 0.25 µm df Rtx-5, 5% phenyl phase column, in the first dimension and a 5 m × 0.25 mm; 0.25 µm df Rtx-200, trifluoropropylmethyl polysiloxane column in the second dimension. In addition to the analytical columns, a 2.8 m × 0.100 mm fused silica bleed line was connected to allow flow during the modulation process. Due to the change in the bleed line length the second-dimension flow was changed to 21 mL/min for proper modulation. Calibration took place after the leak was fixed therefore these results were not impacted by the leak. Figure 2.12 shows the two methods of introducing liquid standards for calibration of target VOCs that were used. The first is liquid injections using the Agilent Technologies 7683 Series Injector to inject 1 μL into the GC×GC system and the second is loading sorbent tubes to be thermally desorbed as described in Section 2.2.2. The goal was to see if the two means of introducing the standards would give comparable levels of sensitivity.

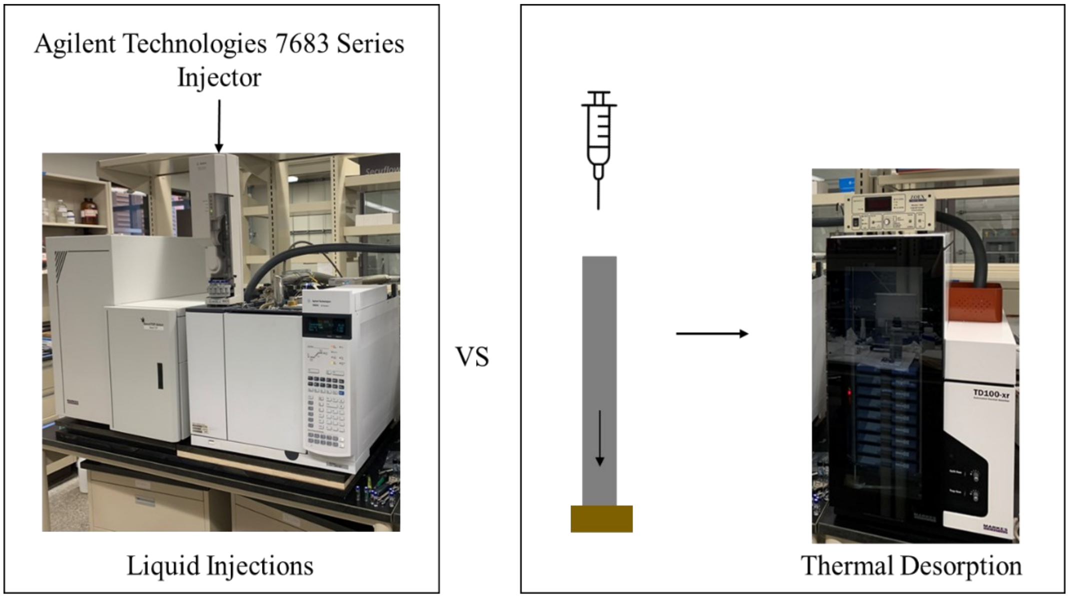


Figure 2.12: Overview of the Two Methods of Introducing Liquids Standards for the Calibration of the Target VOCs

The calibration curves were generated using Microsoft Excel 2016 following data processing on the ChromSpace software using the Extracted Ion Chromatogram (EIC) data from the 70 eV results. The slope and y intercept for the calibration curves were generated using the LNEST function to calculate using the least squares regression formula. The calculated slopes were used along with the standard deviation of the lowest calibration standard to determine the limit of detection (LOD) and limit of quantification (LOQ) for method validation purposes. The LOD values were calculated by taking the standard deviation of the lowest calibration standard, 0.49 mg/L, and multiplying by three then dividing by the calibration curve’s slope. The LOQ values were determined in a similar manner with the standard deviation of the 0.49 mg/L standard being multiplying by ten then divided by the slope of the calibration curve.

n Calibration Data Over the Range of 0.023-0.89 ng on Column

			Liquid Injection						
Compound	^{1}tr (min)	^{2}tr (s)	Slope	Slope Error	y-intercept	y-intercept Error	R^2	LOD (ng)	LOQ (ng)
Ethylene, 1,2-dichloro-, (E)-	6.65	0.79	2.2E+06	4.1E+04	-3.4E+04	1.9E+04	0.993	0.006	0.02
Trichloromethane	6.91	0.72	3.6E+06	5.4E+04	-1.9E+04	2.5E+04	0.996	0.005	0.02
Trichloroethylene	9.21	0.84	2.0E+06	3.7E+04	-1.3E+04	1.8E+04	0.993	0.001	0.004
Propane, 1,2-dichloro-	9.22	1.20	2.8E+06	5.9E+04	-5.4E+04	2.8E+04	0.991	0.02	0.05
Methane, dibromo-	9.34	0.88	1.7E+06	2.1E+04	-2.6E+04	1.0E+04	0.997	0.007	0.02
Methane, dibromochloro-	12.69	0.84	1.6E+06	4.4E+04	-2.5E+04	2.1E+04	0.985	0.03	0.09
Tetrachloroethylene	13.23	0.84	3.6E+06	1.6E+05	-1.6E+05	7.6E+04	0.963	0.0008	0.003
Benzene, chloro-	14.64	1.14	8.0E+06	1.9E+05	-8.5E+04	8.9E+04	0.989	0.004	0.01
Ethylbenzene	15.21	0.97	1.3E+07	3.2E+05	-1.0E+05	1.5E+05	0.989	0.003	0.01
p-Xylene	15.49	0.99	2.1E+07	4.8E+05	-2.5E+05	2.3E+05	0.990	0.003	0.009
Styrene	16.32	1.11	5.9E+06	1.6E+05	-1.1E+05	7.6E+04	0.986	0.001	0.003
o-Xylene	16.39	1.05	1.1E+07	3.2E+05	-1.0E+05	1.5E+05	0.984	0.003	0.008
Ethane, 1,1,2,2-tetrachloro-	17.12	1.05	6.4E+06	1.7E+05	-8.2E+04	8.0E+04	0.987	0.006	0.02
Propane, 1,2,3-trichloro-	17.39	1.34	5.4E+06	1.4E+05	-3.8E+04	6.4E+04	0.988	0.003	0.01
Benzene, (1-methylethyl)-	17.55	0.92	1.6E+07	3.9E+05	-1.3E+05	1.8E+05	0.989	0.004	0.01

^{1}tr- First dimension retention, ^{2}tr- second dimension retention, R^2-
of Detection, LOQ – Limit of Quantificatio

bration Data Over the Range of 0.023-0.89 ng on Column Cont

			Liquid Injection						
Compound	^{1}tr (min)	^{2}tr (s)	Slope	Slope Error	y-intercept	y-intercept Error	R^2	LOD (ng)	LOQ (ng)
Benzene, bromo-	17.84	1.11	5.6E+06	1.4E+05	-5.6E+04	6.4E+04	0.989	0.003	0.009
Benzene, 1-chloro-2-methyl-	18.57	1.07	9.9E+06	3.5E+05	-1.1E+05	1.6E+05	0.977	0.02	0.06
Benzene, propyl-	18.61	0.92	2.0E+07	4.3E+05	-6.7E+04	2.0E+05	0.991	0.007	0.02
Benzene, 1-chloro-4-methyl-	18.75	1.14	1.0E+07	2.7E+05	-1.2E+05	1.3E+05	0.988	0.004	0.01
Benzene, 1,2,4-trimethyl-	19.12	0.91	1.3E+07	2.6E+05	-1.1E+05	1.2E+05	0.992	0.005	0.02
Ethane, pentachloro-	19.44	0.91	1.8E+06	9.8E+04	-9.6E+04	4.6E+04	0.948	0.007	0.02
Benzene, tert-butyl-	19.99	0.93	1.4E+07	2.9E+05	8.0E+03	1.4E+05	0.992	0.005	0.02
Benzene, 1,3-dichloro-	20.48	1.09	8.3E+06	2.0E+05	-1.3E+05	9.4E+04	0.989	0.003	0.01
Benzene, (1-methylpropyl)-	20.61	0.86	1.8E+07	3.7E+05	-8.2E+04	1.7E+05	0.992	0.005	0.02
Benzene, 1,4-dichloro-	20.71	1.09	8.5E+06	1.8E+05	-1.1E+05	8.7E+04	0.991	0.004	0.01
p-Cymene	21.06	0.82	1.6E+07	3.2E+05	-2.2E+05	1.5E+05	0.993	0.002	0.007
Benzene, n-butyl-	22.13	0.87	1.5E+07	3.0E+05	-3.2E+05	1.4E+05	0.993	0.003	0.009
Ethane, hexachloro-	22.82	0.78	2.6E+06	7.4E+04	-4.6E+03	3.5E+04	0.985	0.004	0.01
Propane, 1,2-dibromo-3-chloro-	23.12	1.20	2.4E+06	5.3E+04	-7.0E+04	2.5E+04	0.991	0.002	0.005
Benzene, 1,2,4-trichloro-	26.15	1.07	7.2E+06	1.5E+05	-2.3E+05	6.9E+04	0.992	0.0009	0.003
Naphthalene	26.41	1.27	2.2E+07	4.3E+05	-7.9E+05	2.0E+05	0.993	0.002	0.006
Benzene, 1,2,3-trichloro-	27.28	1.14	7.4E+06	1.5E+05	-1.5E+05	7.0E+04	0.992	0.002	0.006
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	27.29	0.75	4.2E+06	7.7E+04	-2.0E+04	3.6E+04	0.994	0.003	0.01

^{1}tr- First dimension retention, ^{2}tr- second dimension retention, R^2-

of Detection, LOQ – Limit of Quantification n Calibration Data Over the Range of 0.023-0.89 ng on Column

Thermal Desorption									
Compound	^{1}tr (min)	^{2}tr (s)	Slope	Slope Error	y-intercept	y-intercept Error	R^2	LOD (ng)	LOQ (ng)
Ethylene, 1,2-dichloro-, (E)-	6.23	0.54	1.1E+06	1.2E+05	-5.7E+04	5.8E+04	0.812	0.003	0.01
Trichloromethane	7.35	0.66	2.1E+06	1.6E+05	-9.4E+04	7.5E+04	0.904	0.004	0.01
Trichloroethylene	9.66	0.79	1.3E+06	9.8E+04	-8.4E+04	4.6E+04	0.898	0.006	0.02
Propane, 1,2-dichloro-	9.65	1.12	1.8E+06	1.3E+05	-1.1E+05	1.3E+05	0.907	0.008	0.03
Methane, dibromo-	9.75	0.84	1.5E+06	1.2E+05	-9.9E+04	5.7E+04	0.885	0.004	0.01
Methane, dibromochloro-	13.12	0.81	1.5E+06	9.4E+04	-8.8E+04	4.4E+04	0.933	0.002	0.007
Tetrachloroethylene	13.65	0.80	2.8E+06	2.3E+05	-1.7E+05	1.1E+05	0.888	0.005	0.02
Benzene, chloro-	15.05	1.08	5.3E+06	3.8E+05	-3.5E+05	1.8E+05	0.910	0.003	0.01
Ethylbenzene	15.61	0.93	9.3E+06	7.1E+05	-5.9E+05	3.3E+05	0.901	0.02	0.07
p-Xylene	15.89	0.94	1.4E+07	1.1E+06	-9.5E+05	5.1E+05	0.897	0.005	0.02
Styrene	16.71	1.06	3.6E+06	2.6E+05	-2.5E+05	1.2E+05	0.909	0.002	0.007
o-Xylene	16.79	1.00	7.0E+06	5.1E+05	-4.6E+05	2.4E+05	0.906	0.003	0.01
Ethane, 1,1,2,2-tetrachloro-	17.51	1.01	3.0E+06	2.2E+05	-2.1E+05	1.0E+05	0.904	0.006	0.02
Propane, 1,2,3-trichloro-	17.78	1.28	2.3E+06	1.7E+05	-1.7E+05	7.8E+04	0.913	0.004	0.01
Benzene, (1-methylethyl)-	17.92	0.88	1.0E+07	7.6E+05	-6.8E+05	3.5E+05	0.907	0.002	0.006

^{1}tr- First dimension retention, ^{2}tr- second dimension retention, R^2- Linearity, LO
Quantification

ption Calibration Data Over the Range of 0.023-0.89 ng on Column

Thermal Desorption									
Compound	¹tr (min)	²tr (s)	Slope	Slope Error	y-intercept	y-intercept Error	R²	LOD (ng)	LOQ (ng)
Benzene, bromo-	18.22	1.06	2.9E+06	2.0E+05	-2.0E+05	9.2E+04	0.919	0.003	0.01
Benzene, 1-chloro-2-methyl-	18.94	1.02	6.4E+06	4.6E+05	-4.7E+05	2.2E+05	0.909	0.004	0.01
Benzene, propyl-	19.13	0.88	1.7E+06	1.3E+05	-1.2E+05	5.9E+04	0.904	0.002	0.007
Benzene, 1-chloro-4-methyl-	19.13	1.09	5.6E+06	4.0E+05	-3.7E+05	1.9E+05	0.911	0.003	0.01
Benzene, 1,2,4-trimethyl-	19.48	0.87	7.7E+06	6.1E+05	-4.5E+05	2.9E+05	0.893	0.005	0.02
Ethane, pentachloro-	19.81	0.88	1.1E+06	8.4E+04	-8.5E+04	3.9E+04	0.898	0.006	0.02
Benzene, tert-butyl-	20.33	0.89	9.2E+06	6.6E+05	-6.3E+05	3.1E+05	0.911	0.004	0.01
Benzene, 1,3-dichloro-	20.85	1.05	4.9E+06	3.7E+05	-3.4E+05	1.7E+05	0.901	0.004	0.01
Benzene, (1-methylpropyl)-	20.96	0.83	1.1E+07	-7.4E+05	-7.4E+05	3.8E+05	0.900	0.003	0.009
Benzene, 1,4-dichloro-	21.06	1.05	5.0E+06	3.8E+05	-3.4E+05	1.8E+05	0.903	0.006	0.02
p-Cymene	21.41	0.80	9.7E+06	7.4E+05	-6.7E+05	3.5E+05	0.900	0.003	0.01
Benzene, n-butyl-	22.48	0.85	8.5E+06	6.4E+05	-5.8E+05	3.0E+05	0.902	0.005	0.02
Ethane, hexachloro-	23.18	0.77	1.2E+06	8.8E+04	-8.3E+04	4.1E+04	0.902	0.0009	0.00
Propane, 1,2-dibromo-3-chloro-	23.47	1.15	1.5E+06	1.2E+05	-1.1E+05	5.7E+04	0.883	0.002	0.006
Benzene, 1,2,4-trichloro-	26.47	1.03	4.2E+06	3.0E+05	-2.5E+05	1.4E+05	0.909	0.005	0.02
Naphthalene	26.74	1.23	1.2E+07	9.5E+05	-7.9E+05	4.5E+05	0.895	0.009	0.03
Benzene, 1,2,3-trichloro-	27.59	1.11	4.4E+06	3.1E+05	-2.8E+05	1.5E+05	0.911	0.007	0.02
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	27.61	0.73	2.5E+06	1.7E+05	-1.4E+05	8.0E+04	0.918	0.008	0.03

^{1}tr- First dimension retention, ^{2}tr- second dimension retention, R^2- Linearity, LOD
Quantification

Tables 2.4 and 2.5 provide the calibration data for VOCs of interest as well as statistics for select values as well as the LOD and LOQ values for the different compounds. The response levels seen in the two modes of sample introduction were different from each other leading to differences in slope and y-intercept values as well as the linearity. For the range examined here the liquid injection slopes were generally higher than the slopes for the thermal desorption method. Similarly, the error values for the slope and the y intercept are greater for the thermal desorption method which can be related to any differences in the responses between the replicates of the standards used in this method. Here despite performing calibration work after the leak was repaired there were lower values seen with the thermal desorption work which could be connected to slight differences with the split flow between standards. However, the major benefit of the thermal desorption method from an analytical standpoint can be seen by examining the sensitivities of the two sample introduction methods. For several of the VOCs examined here the thermal desorption method showed lower limits of detections compared to the liquid injection method. Other compounds showed a comparable LOD for thermal desorption compared to the liquid injection method which shows that there is no significant loss of sensitivity for those compounds of interest. The LOQ values show a similar trend as many of the VOCs used here showed a decrease in LOQ value in the thermal desorption method with others being relatively comparable. The sensitivity increase seen by the TD-GC×GC method is an advantage for environmental monitoring laboratories as it will enable target compounds to be detected at lower amounts compared to standard methods. The thermal desorption LOD and LOQ values were compared to previous work using thermal desorption coupled to gas chromatography or comprehensive two-dimensional gas chromatography.

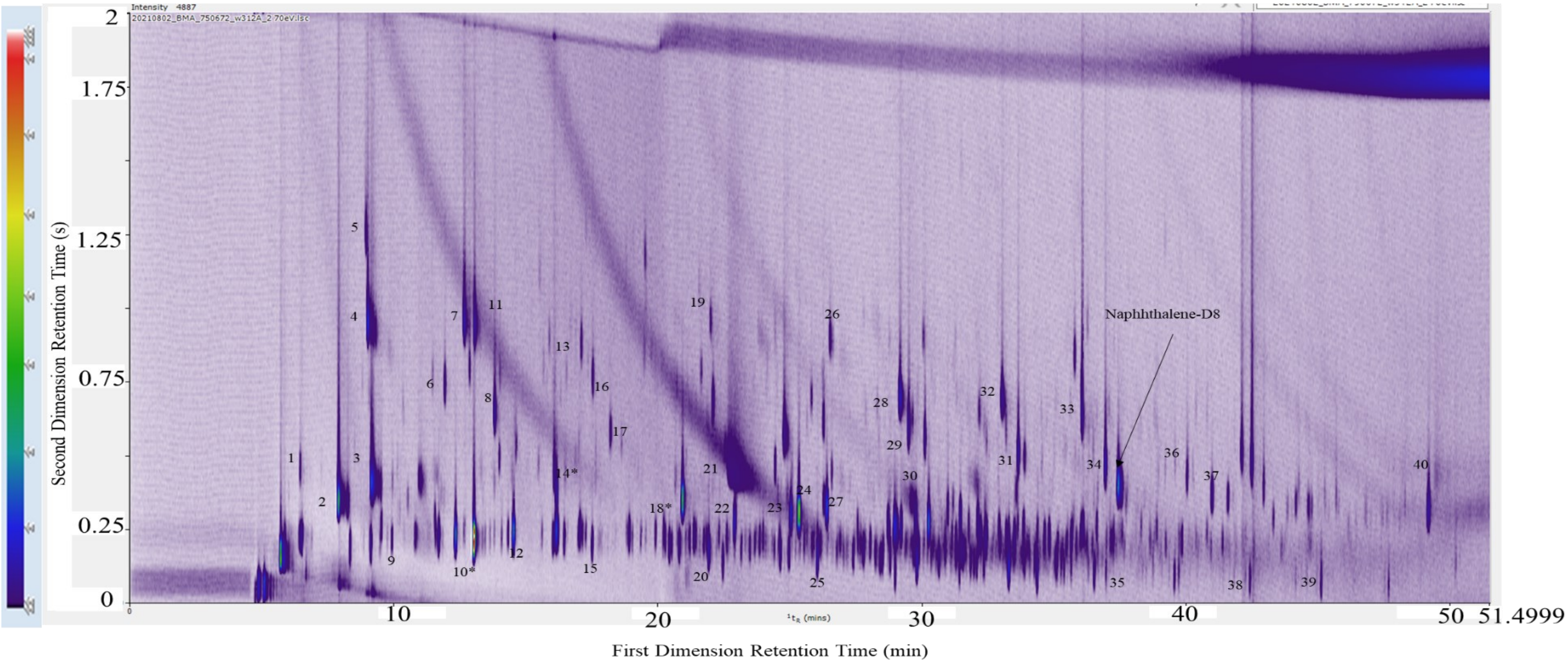
Looking at previous studies' LOD and LOQ work, Wong et al. looked at determining 48 VOCs which showed LODs ranging from 0.01 ng to 1.31 ng using TD-GC-MS which is greater than the LODs calculated in this thesis which range from 0.0009 ng on column to 0.02 ng on column.[156] LOQs in Wong et al.'s work range from 0.02 ng to 2.24 ng which are also greater than the LOQs determined in this thesis which range from 0.003 ng on column to 0.07 ng on column.[156] The decrease in the LOD and LOQ values in thesis shows an advantage of this method which is the increase in sensitivity. Both the zone compression of the modulator as well as the increased separation power of the GC×GC system aides in makes these better detection limits possible. Veenaas et al. used a Gerstel thermal desorption system coupled to a cryogenically modulated GC×GC and high resolution TOFMS.[111] Veenaas et al.'s work showed LODs between 12 pg to 800 pg (0.012 ng to 0.8 ng) which is comparable to some of the LOD values founds here.[111] However, this work showed several VOCs with LODs lower than the Veenaas et al.'s lowest LOD value.[111] The difference in calibration range may be related to some of the differences between literature values.

Ribes et al. used TD-GC-MS to detect 45 ambient VOCs and some of the LODs that the authors were able to determine were comparable to those found in this work.[115]There are several compounds in this work having lower detection limits than those in Ribes et al.'s study such as styrene, 1,2,4-trimethylbenzene, tetrahydrofuran and propylbenzene.[115] Marcillo et al. in their 2017 work had an average LLOQ of 0.94 ng per tube for the 33 compounds of interest.[157] One of the compounds included was xylene and the LLOQ was 0.05 ng per tube which was greater than the LOQ values for both xylenes featured in this work, 0.02 ng on column and 0.01 ng on column.[157] It is important note that many works mentioned here featured benzene and toluene among their calculations though these compounds were not included in this thesis. The reason for benzene and toluene's exclusion is the fact that these compounds were seen in the sorbent tube blank runs as artifacts from the sorbent. Since these were artifacts in the sorbent tubes, calibration curves could not be accurately made as the amount present in the sorbent tubes used for constructing the calibration curves may not be consistent. This would lead to inconclusive results for the LODs and LOQs of benzene and toluene. Overall, the limits of detection and quantification calculated in this work were generally lower than the ones found in literature which shows an advantage for trace level analysis. The calibration curves generated with the thermal desorption data were used for quantification in Chapter 3.

2.3.4 Nontargeted Quantification

The separation power offered by comprehensive two-dimensional gas chromatography allows for nontargeted analysis which is a key part of the hybrid method developed in this work. Chapter 3 will explore the benefits of the nontargeted portion of the developed method, however, the ability to quantify these compounds not from the target lists can be very useful. In this regard, it is important to note that environmental samples can have a large number of compounds present which makes obtaining standards for all compounds impossible.[158] Here the response factors from the target compounds and the concentration of the target compound can be used to quantify the VOCs not on the target list. An early work in air quality monitoring used both external calibration and response factors relative to the response factor of toluene using a TD-GC-MS-FID-sniffer system.[159] The response factors were used in this work due to the large number of compounds present making external calibration for all compounds impossible according to the authors.[159] In this 1995 work, it was seen that quantification via both methods were comparable to each other for hydrocarbons.[159] A similar process is presented here to quantify the nontarget compounds present in air samples.

Here a target compound present in a sample is quantified using external calibration, then the response factors of the both the target and nontarget compounds are used to determine the concentration of the nontarget compound. Therefore, to determine the concentration of a nontarget compound, the information needed is the responses of the target and nontarget compounds as well as the concentration of a target compound. The hybrid targeted-nontargeted method includes a FID detector which gives uniform responses for analytes entering the detector. Therefore, the responses from the FID can be used quantify nontarget VOCs present in samples and to do this a compound from the target list must be present in the sample.



1. Acetaldehyde
2. Ethanol
3. Isopropyl Alcohol
4. Acetone
5. Butanenitrile
6. Methacrolein
7. Methyl Vinyl Ketone
8. Ethyl Acetate
9. Carbon Disulfide
10. Hexane*
11. 2-Butanone
12. Cyclopentane, methyl
13. 2-pentanone
14. Benzene*
15. Heptane
16. Pentanal
17. 1,4-dioxane
18. Toluene*
19. Cyclopentanone
20. Octane
21. Pyridine
22. Tetrachloroethylene
23. Ethylbenzene
24. m-xylene
25. Nonane
26. Cyclohexanone
27. o-xylene
28. Benzaldehyde
29. Octanal
30. Benzene, 1,2,4-trimethyl
31. Nonanal
32. Acetophenone
33. Diethylfumerate
34. Decanal
35. Tridecane
36. Undecanal
37. Naphthalene, 1-methyl
38. Tetradecane
39. Pentadecane
40. Diphenyl sulfide

*- Known Artifacts Compounds

Figure 2.13: GC×GC-TOFMS Chromatogram of a Harynuk Laboratory Chemical Storage Room

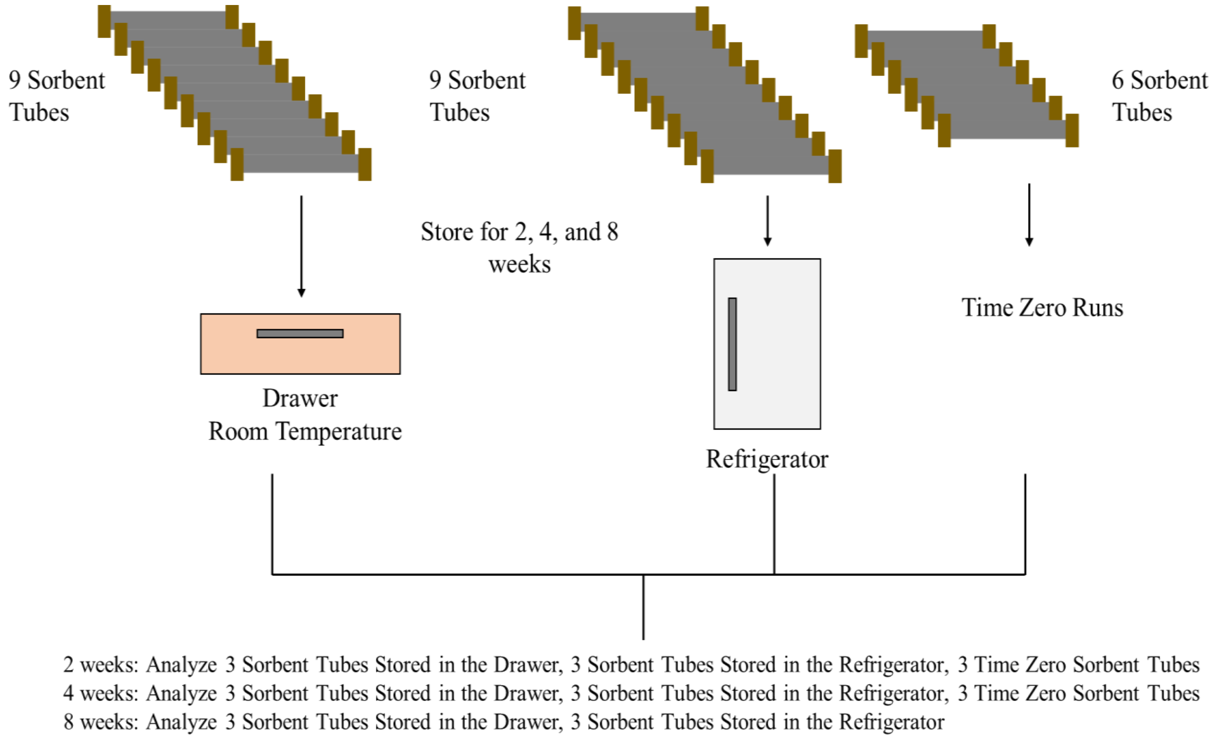
Here the TOFMS response of an air sample collected in the Harynuk Research Laboratory Chemical Storage Room is shown in Figure 2.13 and many of the compounds seen are not from the target compounds list. A more in-depth discussion of this sample is in Chapter 3 in Section 3.3.2.1, but here it is an example of how nontarget quantification works. As an example, one of the compounds in the sample was nonane which is known to cause irritation and headaches if it enters the body.[160] Using the FID response from o-xylene in the sample, the mass of nonane present can be found using $C_{nonane} = \frac{FID\ Peak\ Area\ Nonane}{FID\ Peak\ Area\ o{-}Xylene} \times C_{o-Xylene}$. Here the FID response of nonane was found to be 1.32×10^6 while FID response of o-xylene was 3.36×10^6 and the mass of o-xylene on column was found to be 0.23 ng on column. Using these values, the mass of nonane was determined to be 0.09 ng on column. Converting these into standard EPA units, parts per billion volume (ppbv), o-xylene was determined to be 0.37 ppbv in the air while nonane was determined to be 0.12 ppbv in air. Additional nontarget compounds quantified using this method were ethyl acetate which had a concentration of 0.22 ppbv in air, nonanal determined to have a concentration of 0.18 ppbv and benzaldehyde which had a concentration of 0.40 ppbv in air. All of these were quantified using the response factors relative to o-xylene.

To evaluate this manner of quantification, three target VOCs were quantified with external calibration using the FID data and then they were treated as nontargeted compounds to be quantified using response factors. The three VOCs chosen were o-xylene, ethylbenzene, and tetrachloroethylene with the latter two being quantified relative to o-xylene while o-xylene was quantified relative to ethylbenzene. o-Xylene was determined to have a concentration of 0.37 ppbv in air using the external calibration method. When the response factor method was used, the concentration was found to be 0.40 ppbv. Here the two values differ by 0.03 ppbv which would indicate that the response factor method is relatively accurate compared to the external calibration method. The ethylbenzene results showed a similar trend with the external calibration method giving a concentration of 0.23 ppbv in air while the response factor method gave a concentration of 0.21 ppbv. Here the difference between the two values is 0.02 ppbv which would indicate that the two methods are comparable. However, tetrachloroethylene showed a different trend as the external calibration method gave a concentration of 0.25 ppbv while the response factor method gave a value of 0.04 ppbv. The reason for this is not completely clear, though it could be related to the fact that this compound is halogenated giving it a different response factor compared to hydrocarbons.

Using the FID response data, the concentrations of nontarget compounds can be determined without external standard calibration curves. This is done using response factors of the target analytes and quantifying the nontarget compounds relative to the target compounds. This can be applied to other nontarget compounds present in any air samples collected. As shown here, if target compounds of a similar class are present in the calibration range, then the response factor method can be used for quantifying nontarget VOCs. It is important to note that values for nontarget quantification were impacted by the leak therefore the values determined here are likely not representative of the actual concentrations in the sampled air.

2.3.5 Examination of Sorbent Tube Storage

To preserve the sample integrity, it is important to study the impact storage has on analyte response. A study was done to see the effect of storage time on the analysis using a series of sorbent tubes stored for various lengths of time then determining the effect of the storage on analyte peak area. Here the goal of the study was to see how long multisorbent tubes could be stored before analyte loss occurred. For this study, two sets of nine Universal multisorbent tubes were loaded using the procedure described in Section 2.2.2 to load 1.0 µL of the EPA standard mixture resulting in 0.24 ng on column using a 10:1 split ratio. Volumes loaded onto the sorbent tubes ranged from 0.90 µL for three of the sorbent tubes with the remaining tubes having 1.0 µL loaded onto them. The difference in the volume could lead to variations in the analyte responses between the replicates. Two sets of three freshly spiked sorbent tubes were also run as time zero analyses to compare to the stored sorbent tubes. Figure 2.14 shows the design of the storage study experiment as previously described. The two storage conditions examined are shown in Figure 2.14, the storage time and the storage temperature. The eighteen sorbent tubes loaded with standard were used to determine how the analyte response changes with storage time. One set of nine sorbent tubes went to room temperature storage in the drawer while the other set were placed in refrigerated storage as shown in Figure 2.14. The six sorbent tubes used for comparison purposes as time zero runs were not stored for any period of time. A second goal was to see if the storing the sorbent tubes in a refrigerator would improve the responses at longer storage times.



2 weeks: Analyze 3 Sorbent Tubes Stored in the Drawer, 3 Sorbent Tubes Stored in the Refrigerator, 3 Time Zero Sorbent Tubes
4 weeks: Analyze 3 Sorbent Tubes Stored in the Drawer, 3 Sorbent Tubes Stored in the Refrigerator, 3 Time Zero Sorbent Tubes
8 weeks: Analyze 3 Sorbent Tubes Stored in the Drawer, 3 Sorbent Tubes Stored in the Refrigerator

Figure 2.14: Design of the Storage Study to See the Effect of Storage Time and Storage Temperature on Analyte Response

The time zero sorbent tubes had a similar range of standard spiked onto to them and one set was run with the week 2 samples while the second set was run with the week 4 samples. However, the leak discovered after the study had significant impacts on the results which will be discussed later. The three storage times used in the study (2 weeks, 4 weeks, and 8 weeks) are shown in Figure 2.14 as well. When preparing for storage, the sorbent tubes were tightly capped with brass caps and wrapped in aluminum foil then placed in plastic storage containers. The plastic containers were placed in either the drawer at room temperature or the refrigerator. Following the analysis, the results were processed using the ChromSpace software and the area reports were used for comparing the responses over Microsoft Excel 2016. Average peak area for representative analytes were used to determine if there was any change in response due to storage. In resulting figures, sorbent tubes used for time zero comparisons are labeled as “Time Zero”. For the stored sorbent tubes, the room temperature location is represented by the label “Drawer” and the label “Fridge” represents the sorbent tubes in the refrigerated conditions.

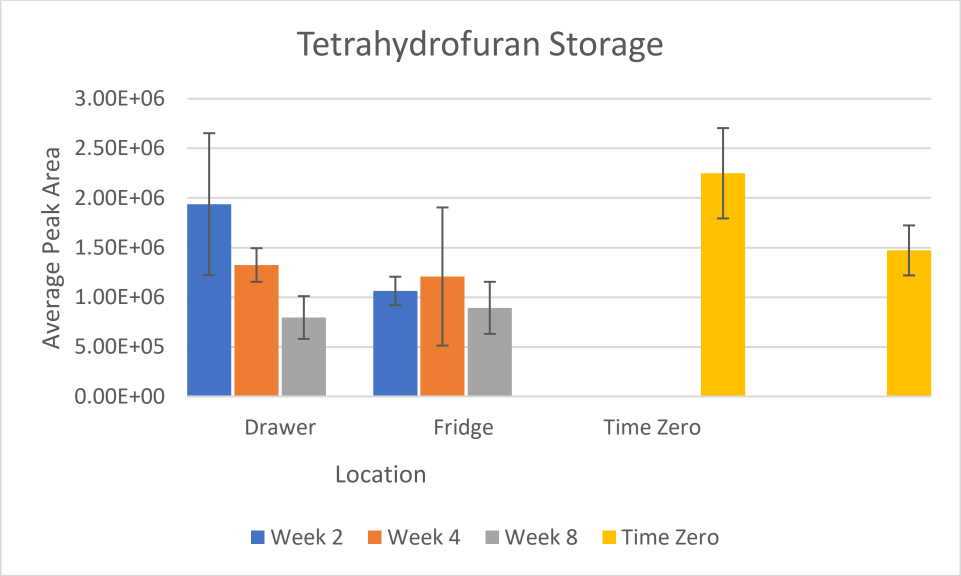


Figure 2.15: Changes in Response of Tetrahydrofuran Over Time in Room Temperature and Refrigerated Locations

One of the representative analytes chosen was tetrahydrofuran as it is a volatile compound thus it can represent the compounds with a similar volatility. Figure 2.15 gives the change in response of tetrahydrofuran over an 8-week period in both storage locations. Due to the higher response seen in the 2-week storage time, it can be observed that longer storage times leads to analyte loss for more volatile compounds such as tetrahydrofuran on multisorbent tubes. Looking at the results for the 2-week storage, the average response was higher for the sorbent tubes stored in the drawer when compared to the sorbent tubes stored in the refrigerator. However, the sorbent tubes stored longer than 2 weeks showed higher responses when stored in the refrigerator rather than in the room temperature location. At the longer storage times, the responses were higher for the sorbent tubes stored in the refrigerator. The decrease in temperature can reduce the loss of the analyte response over extended storage times. Examining Figure 2.15 indicates that sampled sorbent tubes should not be stored longer than the 2 weeks to avoid loss of volatile analytes.

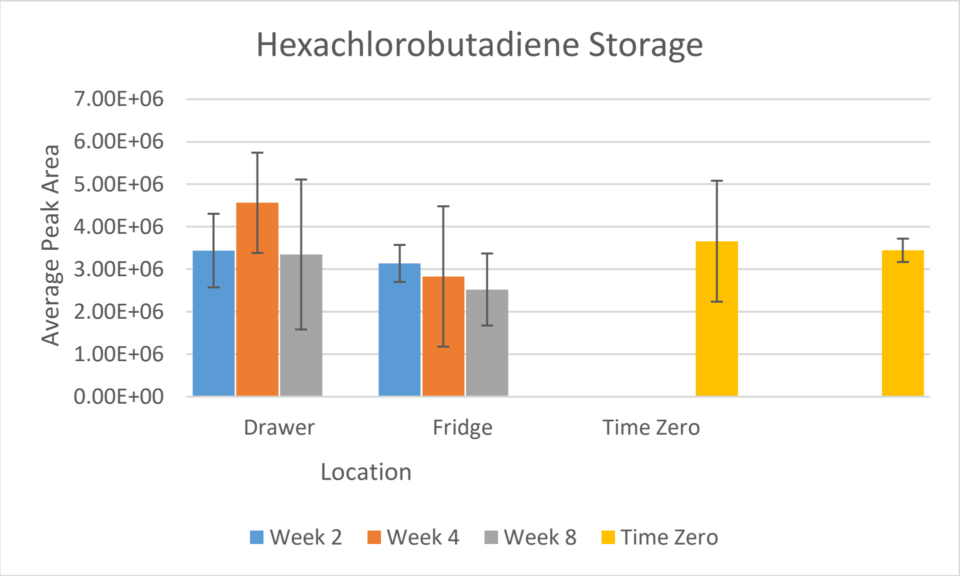


Figure 2.16: Changes in the Response of 1,1,2,3,4,4-hexachloro-1,3-butadiene Over Time in Room Temperature and Refrigerated Locations

1,1,2,3,4,4-hexachloro-1,3-butadiene was used to examine the effect storage on the response of lower volatility compounds which is shown in Figure 2.16. In Figure 2.16, the responses for sorbent tubes stored in both the drawer and the refrigerator are relatively comparable which is unlike Figure 2.15. However, the results from week 4 and week 8 showed high variations which can be connected to the leak discovered in the system. Like tetrahydrofuran in Figure 2.15, the decreased temperature provided by the refrigerated location did not seem to give a major benefit over storage in room temperature conditions. Apart from the 4-week storage at room temperature, the 2-week storage time in both locations showed a greater response over the other storage times. The reason for higher response for this analyte at week 4, is not completely clear but several factors such as human error or the leak could have played a role. Therefore, storing sampled multisorbent tubes for longer than 2 weeks should be avoided to prevent sample loss. Analytes such as 1,1,2,3,4,4-hexachloro-1,3-butadiene are less volatile than compounds such as tetrahydrofuran and there is an additional risk when storing along with the risk of analytes leaving the sorbents. With multisorbent tubes, there is a risk of the less volatile compounds moving to stronger sorbents.[93] As each sorbent is only able to capture a specific range of compounds and desorb them without destruction of the sorbent, migration would prevent those compounds from being desorbed. Semi-volatile compounds can not be effectively desorbed from those stronger sorbents even at increased temperatures. Therefore, this study has shown where the migration of the semi-volatile compounds may occur which is important when planning experiments using multisorbent tubes. Figure A4 and Figure A5 in the Appendix are additional representative compounds which show a similar trend to Figures 2.15 and 2.16. It is important to note that the leak in the system discovered after the study was completed impacted the results due to the sample loss.

Overall, the sorbent tubes stored for 4 weeks in either storage location gave relatively comparable responses while for sorbent tubes stored for 8 weeks generally had higher responses in the refrigerated location. Both locations showed a decrease in response after two weeks of storage for the compounds used in this study. Due to this decrease in response seen after 2 weeks of storage, samples stored on multisorbent tubes should not be stored for longer than 2 weeks to avoid analyte loss. Comparison of the temperature of the storage locations did not indicate any significant benefit to storing the sampled sorbent tubes under refrigerated conditions over room temperature. The fact that storing in the room temperature drawer was comparable to refrigerated conditions may be beneficial in laboratories with limited space in refrigerators. In a commercial laboratory, the loss of analyte to either mitigation or leaving the sorbent can cause inaccurate analysis due to lower responses with longer storage times. To meet governmental regulations, storage time should be minimized to avoid inaccurate reports as this could lead to compounds being missed or thought to be at safe levels. However, one of the impacts of the presence of the leak was the large standard deviation leading to the large error bars in Figures 2.15 and 2.16. The leak can also be connected to the differences between the two time zero runs as well as deviations from the general trend

Several other authors have explored the that impact storage time can have on sampled sorbent tubes. Brown et al. in 2014 looked at storing multisorbent tubes for 1 week, 2 weeks and 4 weeks with 40 ng to 500 ng of analyte on the sorbent tube.[161] Brown et al. looked at nine compounds due to their connection to material emissions: hexane, 4-methylpentan-2-one, toluene, n-butyl acetate, cyclohexanone, 1,2,3-trimethylbenzene, phenol, 4-phenylcyclohexene and hexadecane.[161] The sorbent tubes in Brown et al.'s study were stored under either room temperature or refrigerated conditions either below 3 % humidity or 40 % humidity.[161] This work showed that storing in room temperature locations was just as good as storing in refrigerated conditions similar to the observation in this thesis.[161] In Brown et al.'s work, it was observed that the sorbent tubes could be stored for four weeks which in longer than seen in this work.[161] Also, it is important to note that some works, such as Brown et al., use a Calibration Loading Rig from Markes International which allows a liquid standard to be introduced onto a sorbent tube using a flow of gas.[161] The use of the Calibration Loading Rig could enable the analytes to be bound to a sorbent which has a volatility range that the analyte falls into giving better stability. Future work can extend into using a calibration set up like the Calibration Loading Rig and see if its usage would improve the calibration process as well as the storage study. There are sources which recommend refrigerated storage due to the previously mentioned migration though it may depend on the studied compounds.[93,161]

Ho et al. in 2018 examined the optimization of a TD-GC-MS method which included the storage of sampled multisorbent tubes.[162] Classes of compounds examined here were alkynes, alkanes, alkenes and aromatics on sorbent tubes stored at either 0 °C or -10 °C.[162] Ho et al. saw that at 0 °C there was significant decline in the relative response after 14 days in all classes, except the alkanes, and recovery had dropped below 90 % at that point.[162] After 21 days in storage, the alkynes, alkenes and aromatics showed a decrease of 36 %, 29 % and 21 % respectively with alkanes remaining stable.[162] The sorbent tubes in the -10 °C storage showed improved storage stability compared to the 0 °C storage temperature however there is still some analyte loss at 14 days.[162] The loss for the alkynes and alkenes is about 15-20 % with aromatic loss at ~10 %.[162] Under the -10 °C storage conditions, the alkanes and aromatics showed minimal loss for the 35 days of storage time tested by Ho et al..[162] Their findings at 0 °C are comparable to the observations in this work as the refrigerated conditions are about 4 °C.[162] This means that the multisorbent tubes can not be stored for longer than two weeks before samples loss is observed. Next steps would be to move to lower temperatures as seen in Ho et al.'s work.[162] In their study, it was seen that in -10 °C conditions the amount of loss did not drop below 90 % until 21 days in storage which can be beneficial in busy environmental monitoring laboratories.[162] It is important to note that the EPA TO-17 method suggests that the samples should be stored under 4 °C and analyzed within 30 days, with some VOCs it is recommended to analyzed within a week.[17]

Generally, the results in this work showed shorter storage times compared to literature. This can be related to several different sources such as the fact that standards were loaded using a Hamilton syringe for liquid injections. Because of the way the standards were introduced, it is likely that many of the analytes did not reach the appropriate sorbents. This would lead to under representation of the analytes on the sorbent tubes. Furthermore, the leak contributed to a loss of analytes during analysis which could have led to the results seen here. For the compounds which did make it to the sorbents, there is the risk that the VOCs migrated to stronger sorbents in the multisorbent tube which could have contributed to the results seen here as well. In contrast, it has been seen that single sorbent tubes can be stored for months with long term storage caps at room temperature as long as the analytes of interest are not chemically active.[93] Therefore, if only one sorbent is needed for the analysis, it can be stored for months as long as it is done properly. Lastly, human error could have contributed to the lower storage times if the caps were not the completely tightened. Considering previous work and the observations in this work, unless the laboratory has access to a refrigerator or freezer with no organic solvents then the sorbent tubes should only be stored for up to two weeks before analysis.[93,161,162] This procedure will prevent significant analyte loss due to migration to stronger sorbents or loss from the sorbent. If refrigerator or better yet freezer space is available without contaminations, then sorbent tubes can be stored for a longer period.

2.4 Conclusions

This chapter has focused on the optimization and development of a hybrid targeted-nontargeted TD-GC×GC-TOFMS/FID method for the analysis of VOCs in air. New methods are needed for environmental air monitoring as the VOCs present in the atmosphere can be incredibly harmful to both the environment and human health.[12] This hybrid method is beneficial to monitoring laboratories as there are compounds present in the atmosphere which are not on target lists which are currently used for air monitoring. To create this method, comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry is utilized. Columns phases and dimensions selected for this method were the Rtx-5 and Rtx-200 to increase separation and allow for unknown compounds, compounds not on the target list, to be seen more easily. Thicker films were chosen as the target analytes of interest are volatile and would have low retention in thinner films which could result in decreased resolution for both target and nontarget compounds.

Optimization of the modulation period was carefully performed into order better utilize the second-dimension space and a smaller modulation period of 2.0 s was selected due to the increased in resolution observed. This increase in resolution was a result in the peaks being properly sampled with the 2.0 s modulation period. Optimization of the thermal desorption conditions lead to complete desorption with the following sorbent tube desorption conditions: desorption time of ten minutes at 250 °C with a desorption flow rate of 50 mL/min. Complete desorption of the focusing trap was seen with a desorption time of 3 minutes at 300 °C with a 20 mL/min split flow during the focusing trap desorption. The inclusion of the split was chosen to allow for increased focusing trap desorption without increasing the pressure significantly as this can lead to instrument damage. While the thermal desorption instrument can be fixed, using a split will increase the time between maintenance and the lifetime of the thermal desorption unit. The split flow was carefully considered to allow for better desorption of the focusing trap and to introduce more of the sample into the GC×GC-TOFMS system for analysis. Sorbent selection for the thermal desorption tubes was done with the goal of sampling both target compounds and unknowns thus a multisorbent tube containing Tenax TA/ Carbograph 1/Carboxen 1003 (or Tenax TA/ Carbograph 1/Carbosieve SIII) was used in this work.

Target compounds were calibrated using the data from the 70 eV responses over the range of 0.023 – 0.89 ng on column with FID responses being used for nontarget quantification. The sensitivity of this method was shown to be able to detect trace amounts of VOCs present in the atmosphere. Limits of detections and limits of quantification found using this method were determine to to be either comparable to previous works or improved. The limits of detection for the target compounds from the EIC responses ranged from 0.0009 ng on column to 0.02 ng on column using thermal desorption. While the limits of quantification ranging from 0.03 ng on column to 0.07 ng on column with thermal desorption. The increase in sensitivity is made possible due to both thermal desorption and comprehensive two-dimensional gas chromatography. The low limits of detection and quantification achieved by this method indicated that the hypothesis for low limits of detection was correct. Nontarget quantification via target compound response factors allows for the concentration of compounds not present in the target lists to be determined. This process enables improved environmental monitoring over using the target lists on their own. Furthermore, there is the potential to expand environmental monitoring through the discovery of new compounds of interest with nontargeted analysis. The ability of hybrid targeted-nontargeted methods to quantify compounds but also provide a more in-depth insight into the samples can be invaluable. Sampled sorbent tubes can be stored up to two weeks in either room temperature or refrigerated storage. Care should be taken with storing sampled multisorbent tubes to avoid mitigation of analytes and these sorbent tubes should be analyzed quickly.[93] The fact that the refrigerated sorbent tubes did not show improved storage compared to the room temperature sorbent tubes shows that hypothesis for this experiment was not correct. Future work can be done to further examine the storage conditions of sorbent tubes. However, the leak did have a significant impact on the results of the study. Because of this leak, the results for nontarget quantification may not be representative of the concentrations at the sample site. Also, the leak led to large variations between the results of the storage study which would indicate instability in storage. Despite the leak, the work done here has provided a method which can be used to determine the presence of target compounds and unknown VOCs which may be present in the atmosphere.

Chapter 3 Applications of a Hybrid Targeted-Nontargeted TD-GC×GC-TOFMS Method

3.1 Introduction

Environmental air monitoring is necessary in numerous applications in both indoor and outdoor settings as humans can be exposed to harmful VOCs in both locations. This common application of thermal desorption can be divided to several sections, two of which being workplace monitoring and ambient air monitoring (both indoors and outdoors).[94] However, one thing holding environmental monitoring back is the usage of target lists as the only possible VOCs of interest. There is the potential for VOCs not monitored by a governmental agency to be present which can be missed with by commercial laboratories. One example of the issue with these lists was the seen in an incident in Pennsylvania in the years 2010-2012.[20] Here compounds from fracking fluid were found in water and commercial laboratories could not find the compound causing the water to foam.[20] In that case without the nontarget capabilities offered by comprehensive two-dimensional gas chromatography, the source of the issue may not have been found. This technique allows for the range of the compounds to be extended and potentially even see all VOCs present in the sample thus new goals can be accomplished.[19,146] It is important to create methods that can see beyond those lists to avoid situations where there is something wrong with the sample, based on physical characteristics, but the results come back negative. Without the increase in separation power provided by comprehensive two-dimensional gas chromatography many peaks may be missed due to coelution or masking which creates a problem for monitoring the VOCs present.[23]

Here various applications of air monitoring are explored using the optimized hybrid method from Chapter 2 to see the target compounds as well as other potential VOCs of interest. Figure 1.5 showed the process for sample collection and the analysis of the sampled sorbent tubes. At the sampling location, the sampling pump is set up and run for an hour.[17] The sorbent tube is then transported back to the laboratory for analysis using the hybrid method. For active sampling with sorbent tubes, the supplies are a sampling pump and the sorbent tubes which simplifies sample collection process compared to other methods. Industrial sources are just one source of airborne VOCs and other possible sources include vehicles and solvents.[163,164] Air samples can be very complex, therefore it is possible that there are compounds present beyond the target compounds which can be difficult to see with current standard methods.[9] The number of activities releasing VOCs in the air ranges from occupational to standard household actions such as cleaning or painting.[165] Having the understanding that normal activities can contribute to VOCs in the air is important for accurate determination of the sources of VOCs. The objective of this chapter was to apply the hybrid method to a variety of locations with different potential sources to see the benefit. Here the hypothesis was that there would be a significant number of nontarget compounds present in the samples. The field samples presented in this chapter show that while the target compounds can be present in the air, there are other VOCs present from a variety of sources. The inclusion of both target and nontarget compounds provides a greater insight into the composition of air samples.

3.2 Experimental

3.2.1 Sampling

Air samples were collected using GilAir-3 sampling pumps (Sensidyne, St. Petersburg, FL, USA) which were calibrated using Gilibrator 2 Calibrator (Sensidyne, St. Petersburg, FL, USA) to set the sampling flow rate. The stainless steel sorbent tubes used had the following dimensions: 89 mm × 6.4 mm × 5 mm which had 6 cm of sorbent packed inside.[90] Sorbent tubes used for sampling were purchased from Markes International (Markes International Ltd., UK) and Camsco (Houston, TX). These sorbent tubes had three sorbents packed from weakest to strongest sorbent, Tenax TA/ Carbograph 1/Carboxen 1003 (or Tenax TA/ Carbograph 1/ Carbosieve SIII). Prior reaching the sampling site, the sampling pumps were calibrated to a flow rate between 49-51 mL/min based on the literature value for optimal sampling flow rate of 50 mL/min.[90,103] Sorbent tubes were loaded with 1 μL of a 4.21 mg/L naphthalene-D8 internal standard to determine potential loss which occurred during the sampling process. Sample times for the following samples was 60 min based on EPA sampling parameters with the start and end times recorded for each sampling site.[17] Figure 3.1 shows the sampling set up for the collection of air samples via active sampling with sorbent tubes. Once at the sampling site, the sorbent tube was connected to an air pump to pull the air through the sorbent tube to collect the VOCs present in the air.

Figure 3.1: Example Sampling Set up Using Sorbent Tubes via Active Sampling for VOCs in the Air

3.2.2 Standards and Solvents

The sampling internal standard was naphthalene-D8 which was prepared in ACS grade methanol (99.8% assay). The standard was prepared from a 1124 mg/L stock solution and the working solution of 4.21 mg/L was prepared using Microman (Gilson Incorporated, WI, USA) positive displacement pipettes to dispense stock internal standard solutions. The mass of solution added was recorded and the density of methanol at the current laboratory temperature was used to determine the actual concentration of the internal standard. When spiking the sampling internal standard onto the sorbent tubes, a Hamilton 10 μL syringe was used to apply standard to the sampling end of the sorbent tube. This was done as shown in Figure 2.1 from Section 2.2.2. The volume was recorded before and after loading to determine the actual volume loaded onto the sorbent. The final volume was subtracted from the initial volume to obtain the actual volume loaded.

The EPA TO-17 method states that the syringes can be used to load standards on to sorbent tubes if a GC inlet could not be used to pass carrier gas through the sorbent tube while loading the standards.[17] In the EPA method, the authors state that the standards should be loaded on the non-sampling end but this would not work for multisorbent tubes.[17] Here loading the standards in the sampling direction works for multisorbent tubes as there is no risk of VOCs being trapped on strong sorbents. There is the risk of VOCs being lost as the standards do not quite reach the proper sorbents and more volatile VOCs may be lost when loading.

3.2.3 TD-GC×GC-TOFMS/FID Conditions

Samples were thermally desorbed in an automated TD unit (TD 100-xr Markes International Ltd., UK) then analyzed in the GC×GC system, an Agilent Technologies 7890 GC. Grade 5.0 helium carrier gas (Linde Canada Inc., Mississauga, ON, CA) was used for both the GC×GC analysis and the TD process. The first-dimension column was a 30 m × 0.25 mm; 1.0 µm Rtx-5 df, 5% phenyl phase column, with the second-dimension column being a 5 m × 0.25 mm; 0.5 µm df Rtx-200, trifluoropropylmethyl polysiloxane column. A 2.5 m × 0.100 mm fused silica bleed line was used which provides an outlet for the carrier gas if the sample loop is over filled and allows for reversed flow.[136] The purge time was set to 0.0 min to prevent analyte loss before desorption then the sorbent tube was desorbed in the tube oven at 250 °C for ten minutes at a flow rate of 50 mL/min. The focusing trap (General Purpose Carbon) was initially held at -25 °C then heated to 300 °C. The maximum temperature of 300 °C was held for three minutes for the injection with a split flow of 20 mL/min. The flow path temperature of the thermal desorption unit was set to 150 °C.

For the gas chromatograph conditions, the initial oven temperature was set to 30 °C then the temperature was ramped at a rate of 5°C/min, optimal heating rate, to a final temperature of 250 °C. The initial temperature was held for four minutes while the final temperature was held for five minutes. Flow rate for the first-dimension column was set to 1 mL/min with the second-dimension flow rate set to 20 mL/min. The modulator used here was the SepSolve INSIGHT reversed fill/flush modulator (SepSolve Analytical Ltd., Peterborough, UK). Modulation period was set to 2.0 s with a fill time of 1.9 s and a flush time of 0.1 s. The second-dimension flow was split between the FID and the Markes BenchTOF-Select (Markes International Ltd., UK). The BenchTOF was set to collect at an acquisition rate of 100 Hz and collected from 40 – 300 m/z. The transfer line temperature was set to 250 °C and the ion source temperature was set to 250 °C. Tandem ionization was employed for this analysis with the two ionizations energies being 70 eV and 12 eV. The filament voltage was set to 1.7 V and the filament delay was set to 460 s for trip blanks. The FID temperature was 300 °C with a helium makeup flow of 20 mL/min, air flow of

250 mL/min and hydrogen flow of 80 mL/min. The TD-GC×GC-TOFMS/FID system was controlled using ChromSpace software version 1.5.1 (SepSolve Analytical Ltd., Peterborough, UK). The instrument conditions used in this chapter were the optimized conditions developed in Chapter 2 and listed in Table 2.1 in Section 2.2.3.

3.2.4 Data Processing

Data processing took place using ChromSpace software version 1.5.1 (SepSolve Analytical Ltd., Peterborough, UK) with curve fitting algorithm used for peak detection with three points used for smoothing. Baseline was set to natural, and region of interest called stencils were used to detect the target compounds. NIST and Wiley mass spectral databases were used for library searching for the identification of compounds. Integration parameters for the overall chromatogram were minimum area, which is the lowest peak area to be detected, minimum height is the lowest peak height to be detected, and the smallest peak width was set using minimum peak width. The minimum area was set to 10000, minimum height of 10000 and minimum width of 0.0100. Parameters for detecting the target compounds were minimum area of 1000, minimum height of 100 and minimum width of 0.0100. Identification parameters were the same as those for integration for peak detection and in addition to those the method used three qualifier ions and uncertainty was set to 50 %. The quantification ions were set for each analyte of interest. The data processing conditions used in this chapter were same as the conditions used in Chapter 2 and listed in Table 2.2 in Section 2.2.4.

3.3 Results and Discussion

3.3.1 Outdoor Air Samples

Sampling sites were chosen to obtain a diverse range of compounds to show the nontarget analytes present. Outdoor sampling sites included construction sites, public parks, roadsides, and bus stations. These locations are known to have VOCs from vehicle exhaust or from nearby industrial sources. After loading the internal standard, the sorbents tubes were tightly capped with brass caps and wrapped in aluminum foil then placed in a plastic container for transport. A trip blank was included to account for any VOCs which may enter the sorbent tubes during transport. When sampling was complete, the caps were resealed on both ends of the sorbent tube then the aluminum foil was wrapped around the sampler before being placed in back in the container. Sampled sorbent tubes were analyzed upon returning to the laboratory after sampling was completed. Each site had duplicate samples collected using the same conditions for sampling though flow rate may have been slightly different.

An internal standard of naphthalene-D8 was used to determine if any loss that occurred during sampling. Naphthalene-D8 was selected as it does not naturally occur in the atmosphere. The concentration was selected to be in the range of the compounds of interest so not to impact the responses of nearby analytes. Therefore, the concentration of the internal standard was 4.21 mg/L and three replicates of 1.0 μL of solution were spiked onto sorbent tubes and analyzed prior to any sampling taking place. The areas of these internal standard runs were 1.11×10^6, $1.04 \times 10^6$and 5.98×10^5. Based on these results, any areas less than these values would indicate that there was loss of internal standard during sampling. Internal standard loss is an indication that there was loss of analyte during the sampling process as well. It is critical to state that these values may have impacted by the leak. As a result, any determination in sampling loss may not be completely accurate due to the variations in these responses. Compound identifications were based on mass spectral library searching using the data files from the 70 eV results with retention index (RI) values included as well. Calculated RI values were compared to literature RI values from the NIST databases or PubChem.

The samples run in this chapter were also impacted by the leak mentioned in Chapter 2 which led to differences in the responses between replicates collected at the same sample site. Because of this difference in replicate responses, the replicate with the highest response was shown in this chapter. This also makes it difficult to determine if sample loss took place as lower peak areas of the internal standard may be linked to the leak and not a result of sample loss. The presence of this leak impacts any quantification as the amount present at the site may be greater than what was found in the sampled sorbent tubes. As a result, the data would underrepresent the concentrations present in the sample which is problem when reporting this information as it could lead to the risk if VOCs presenting a health hazard are falsely determined to be at a safe level.

3.3.1.1 University of Alberta Bus Station

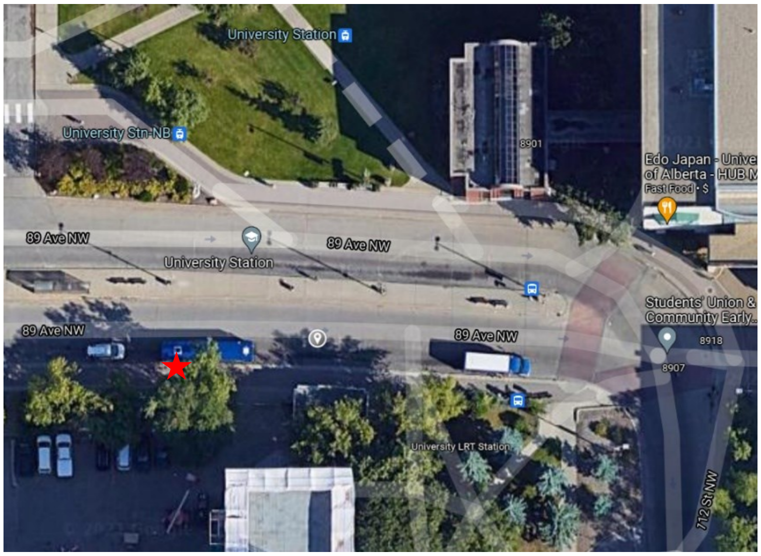
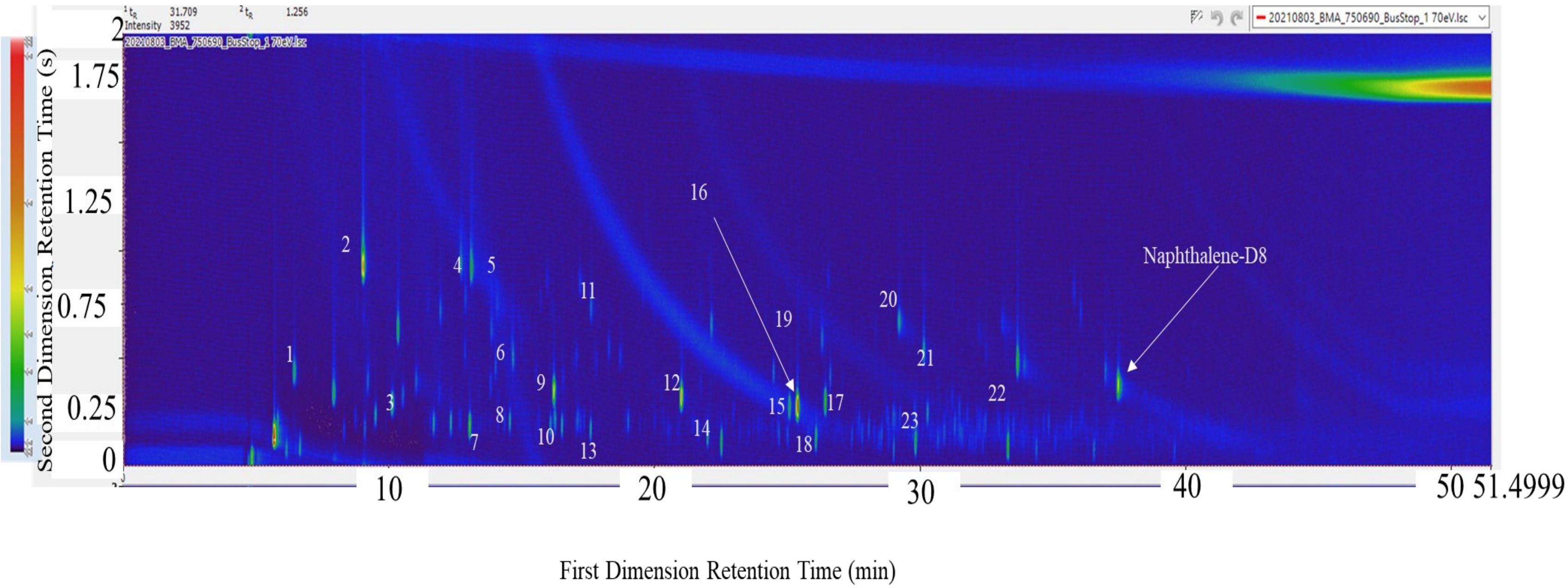


Figure 3.2: University of Alberta Bus Station - Image taken from Google Maps[166]

One of the outdoor sites sampled was the University of Alberta bus station, located outside HUB Mall at the University of Alberta in Edmonton, AB, CA. This site is shown in Figure 3.2 via Google Maps and the red star on the map shows where the sample was collected.[166] The sampling took place during the late afternoon where Edmonton Transit Service buses would idle when waiting for passengers. Sampling took place in the summer on August 3, 2021, from 2:29 pm to 3:29 pm and the temperature at the time was 27 °C. During the sampling time, it was a sunny afternoon with a slight breeze in the area. Buses would drive by the sampling site and there was almost always a bus idling in front of the sampling pump. The sample pumps connected to the sorbent tubes were placed a short distance from each other with one on a bench and the other placed on ground near the bench with the other sampling pump. The sample pump was calibrated to collect at a rate of 50.12 mL/min for 60 minutes which would give 3.01 L of air collected.

Due to the exhaust from the idling and passing buses, aromatic compounds such as ethylbenzene and the xylenes are to be expected to be in the air due to their presence in fuels.[164]

Figure 3.3 shows the separation of the 60-minute sample collected at the sampling site. The color bar on the left side of the figure indicates the intensity of the analytes present in the sample. Below the chromatogram in the figure is a list of some of the compounds identified by mass spectral library searching. The compounds shown in the figure were some of the more abundant compounds present in the sample. In Figure 3.3, benzene, hexane, and toluene have asterisks by their name as these are found in sorbent tube blanks as artifacts and this would be true all samples. The presence of these compounds in the chromatogram does not entirely mean these VOCs were at the sample site as they are being produced from sorbent use. These compounds can still be present in the atmosphere, but the analyst needs to take into consideration the fact that these will always be present to some degree after the sorbent has been used.



1. Acetaldehyde
2. Acetone
3. Methane, ido-
4. Methyl Vinyl Ketone
5. 2-butanone
6. Tetrahydrofuran
7. Hexane*
8. Methylcyclopentane
9. Benzene*
10. Pentane,2,3-dimethyl-
11. Pentanal
12. Toluene*
13. Heptane
14. Octane
15. Ethylbenzene
16. m-xylene
17. o-xylene
18. Nonane
19. Heptanal
20. Benzaldehyde
21. Octanal
22. Nonanal
23. Benzene, 1,2,4-trimethyl-

*-Known Artifacts

Figure 3.3: GC×GC-TOFMS Chromatogram of the University of Alberta Bus Station Air Sample

Table 3.1: University of Alberta Bus Station Air Sample Total Ion Chromatogram Data from TOFMS Results

Compound Name	^1t_r (min)	^2t_r (s)	Area	Height	Width	Similarity	Reverse	RI	Lit. RI
Acetaldehyde	6.43	0.43	9.86E+05	2.73E+04	0.3323	909	946		
Ethanol	7.91	0.33	1.21E+06	3.00E+04	0.3004	880	940		
Acetone	9.02	0.92	4.65E+06	1.26E+05	0.3331	947	952		
Methane, iodo-	10.13	0.29	5.96E+05	3.38E+04	0.1334	923	951	525.61	530
Pentane, 2-methyl-	11.67	0.19	2.20E+05	1.64E+04	0.1329	807	892	564.72	559
Pentane, 3-methyl-	12.32	0.19	3.96E+05	1.74E+04	0.167	785	866	581.32	580
Methyl vinyl ketone	12.69	0.93	7.52E+05	1.49E+04	0.2335	781	910	590.74	606
n-Hexane	13.04	0.18	1.35E+06	6.01E+04	0.2335	897	925	600	600
2-Butanone	13.09	0.91	1.57E+06	3.85E+04	0.2998	807	873	600.77	601
Tetrahydrofuran	14.66	0.50	4.76E+05	1.31E+04	0.1996	731	947	635.36	621
Hexane, 2-methyl-	16.08	0.18	3.67E+05	1.64E+04	0.1671	796	854	666.73	659
Benzene	16.21	0.34	2.25E+06	9.20E+04	0.2999	926	941	669.70	662
Pentane, 2,3-dimethyl-	16.26	0.21	2.01E+05	1.48E+04	0.1334	674	839	670.84	675.8
Hexane, 3-methyl-	16.51	0.18	3.99E+05	1.88E+04	0.1671	826	888	676.33	667

Heptane	17.58	0.16	4.07E+05	1.61E+04	0.1671	796	861	700	700
Cyclohexane, methyl-	18.99	0.20	2.71E+05	1.07E+04	0.1668	758	864	732.08	713
Toluene	21.01	0.32	2.85E+06	1.26E+05	0.3334	891	903	777.84	769
Octane	21.99	0.14	5.93E+05	2.49E+04	0.2004	846	915	800	800
Ethylbenzene	25.07	0.27	7.97E+05	3.11E+04	0.1668	745	899	876.02	864.1
m-Xylene	25.37	0.27	4.53E+06	1.68E+05	0.4661	899	942	883.33	872.5
Nonane	26.07	0.13	7.64E+05	3.06E+04	0.1673	804	873	900	900
Heptanal	26.29	0.58	4.26E+05	1.04E+04	0.2667	732	803	906.45	901
o-Xylene	26.42	0.29	1.24E+06	4.61E+04	0.2003	870	902	909.75	908
Benzaldehyde	29.19	0.67	9.10E+05	1.94E+04	0.2997	818	895	983.64	972
Benzene, 1,2,4-trimethyl-	29.22	0.23	1.49E+05	5.24E+03	0.1664	632	731	984.44	976
Decane	29.82	0.11	8.13E+05	3.29E+04	0.1671	818	868	1000	1000
Octanal	30.12	0.53	6.67E+05	1.75E+04	0.2331	815	898	1009.08	1005
Benzene, 1,4-dichloro-	31.19	0.31	91177.39	4.15E+03	0.2342	632	677	1040.11	1021.24
o-Cymene	31.29	0.18	2.73E+05	8.71E+03	0.1336	694	761	1042.99	1026
Benzene, 1-ethyl-2,3-dimethyl-	32.43	0.19	2.54E+05	7.33E+03	0.167	691	762	1075.95	1094
Undecane	33.29	0.09	1.10E+06	4.70E+04	0.167	842	882	1100	1100
Nonanal	33.65	0.48	1.56E+06	4.60E+04	0.2334	826	849	1112.06	1102

Naphthalene-D8	37.45	0.37	2.90E+06	8.41E+04	0.466	858	905		

$^{1}t_r$ – First dimension retention time, $^{2}t_r$ – Second dimension retention time, RI – Retention index, Lit. RI – Literature Retention Index

The compounds shown in Figure 3.3 as well as the chromatogram itself gives insight into the benefit of nontargeted analysis. While Table 3.1 has a more detailed list of the compounds present in the sample, here many of the compounds found in the sample not a part of the target list which were used to make the calibration curves in Chapter 2. While compounds such as the aldehydes and alkanes would be missed in traditional analysis and for cases where harmful VOCs or products from these VOCs are present this is an issue. Table 3.1 gives a more comprehensive look into the VOCs present at the University of Alberta Bus Station with both similarity and reverse match factors and retention indices (RI) included for increased identification. Looking at the mass spectral match factors, generally the compounds found have values greater than 700 which can indicate the compound is good match compared to library. Compounds such as 3,3-dimethylpentane, 1,4-dichlorobenzene and o-cymene have lower values which could indicates the identity of these compounds could be different. The early compounds, ethanol, acetone and acetaldehyde, do not have RI values due to the alkanes ranging from pentane to hexadecane. RI values were compared to the known values with the compounds having the most significant differences from known retention index values were 1,4-dichlorobenzene, o-cymene and methylcyclohexane. Like Figure 3.3, most of the VOCs seen in Table 3.1 were not among the target list compounds presenting a short coming in the current methods. Looking at the napthaplene-D8 internal standard, the area is 2.90×10^6 in this sample which is greater than initial tests despite have the same volume spiked on. The fact that this value not less than the values states previously would indicate that there was no sample loss that occurred during sampling.

The thermal desorption calibrations performed in Chapter 2 can be used to quantify the target compounds present in the sample. The calibrations were performed using the extracted ion results and these were used for quantification here. At this sampling site there was 0.31 ppbv of tetrahydrofuran present in the air. Looking at other target compounds, ethylbenzene was present in the air at a concentration of 0.15 ppbv in the air at the bus station while o-xylene was at a concentration of 0.19 ppbv. These compounds were found at lower concentrations than the EPA range which is 0.5 ppbv to 25 ppbv and the lower range seen in this method can be beneficial if it is desirable to measure lower concentrations. It is possible the VOCs were present at higher concentrations but the leak in this system has led to a loss of analytes during the analysis. Therefore, the values listed here are not representative of the actual concentration in the air.

The presence of ethylbenzene as well as the xylenes was expected and can be related to the gasoline use by the buses both driving through the station and idling.[1,167] While benzene and toluene are a significant part of fuel emissions and are in the sample, seen in both Figure 3.3 and Table 3.1, these are artifacts from the sorbent and their presence in the sample can not be linked solely to the sampling site.[164,167,168] While the sorbent use can contribute to the response for benzene and toluene, both ethylbenzene and o-xylene had responses lower than toluene and benzene which is consistent with previous work.[164] m-Xylene showed a higher response compared to the other BTEX compounds but another isomer of xylene, p-xylene, elutes at the same time which can lead to higher responses.[169] Compounds such as acetaldehyde, 2-butanone, heptanal, octanal, nonanal and benzaldehyde have been previously detected at bus stations and other exhaust sources.[170,171] Several lighter alkanes, branched and straight chain, were seen in the bus station air sample as a result of fuel emissions which is consistent with Sagebiel et al.'s work using TD-GC.[171] Standard methods would have left the aldehydes and alkanes unreported as these are a not part of the target lists. Compounds such as acetaldehyde and nonane present increased risk of irritation as a result of exposure and while these symptoms may be minor, it is still important to have a full understanding of all the VOCs present in the sample.[160,172]

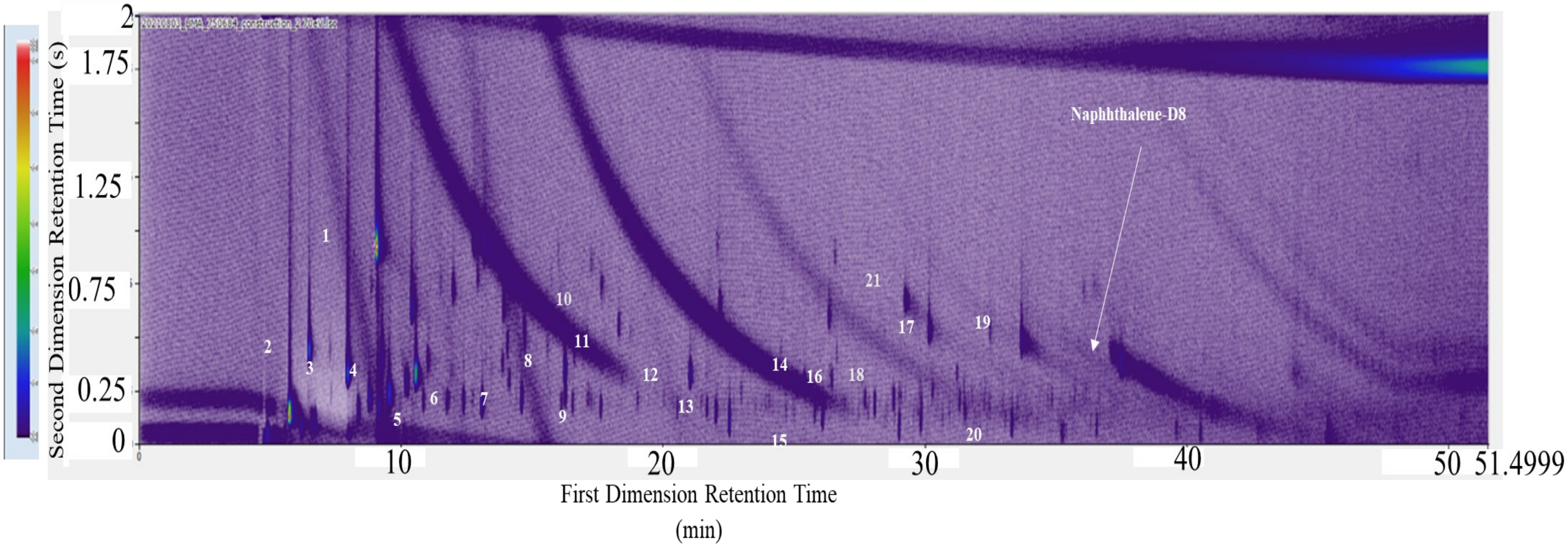
3.3.1.2 University of Alberta Construction Site

Figure 3.4: University of Alberta Dentistry/Pharmacy Construction Site Sampling Location - Image from Google Maps[166]

Construction is common at the University of Alberta, Edmonton AB, CA, which presents the potential for VOCs to be introduced to the air. One such example was the construction taking place at the Dentistry/Pharmacy Building and the sampling site was a short distance from this construction site. Figure 3.4 shows the sampling location in an image from Google Maps and the red box is used to show the area closed off for construction.[166] The red star in Figure 3.4 is show the general area where sampling took place at this location. This sample was collected in the summer on August 3, 2021, from 3:31 pm to 4:41 pm. The sampling pump was calibrated to sample at a rate of 50.33 mL/min for 60 minutes giving 3.01 L of sample collected. The sampling pumps were placed on a nearby bench under some trees a short distance apart with the construction taking place.

The resulting chromatogram is shown in Figure 3.5 which includes a list of the most abundant VOCs present in the sample. The color bar on the left side of Figure 3.5 indicates the intensity of the peaks and the compounds shown were some of the most abundant peaks present.

Construction activities typically involve fuel combustion from some of the tools used which can lead to aromatic compounds being introduced and the vegetation nearby presents the possibility of biogenic compounds. Therefore, these classes of compounds can be expected in the sample because of these activities.



1. Acetone
2. Acetaldehyde
3. Ethanol
4. Methane, ido-
5. Pentane, 3-methyl-
6. Hexane*
7. Cyclopentane, methyl-
8. Benzene*
9. Heptane
10. Pentanal
11. 1,4-dioxane
12. Toluene*
13. Octane
14. m-xylene
15. Nonane
16. o-xylene
17. Octanal
18. Camphene
19. Nonanal
20. Undecane
21. Benzaldehyde

*- Known Artifacts Compounds

Figure 3.5: GC×GC-TOFMS Chromatogram of an Air Sample Collected at the University of Alberta Dentistry/Pharmacy Construction Site

Table 3.2: University of Alberta Dentistry/Pharmacy Construction Site Total Ion Chromatogram Data from TOFMS Results

Compound Name	^1t_r (min)	^2t_r (s)	Area	Height	Width	Similarity	Reverse	RI	Lit. RI
Acetaldehyde	6.48	0.43	3.15E+06	1.17E+05	0.3334	959	961		
Ethanol	7.95	0.33	3.41E+06	1.07E+05	0.3669	930	931		
Acetone	9.05	0.92	1.52E+07	5.36E+05	0.3332	937	942		
Pentane	9.14	0.17	1.02E+06	3.36E+04	0.2665	788	869	500	500
Isopropyl Alcohol	9.26	0.39	6.97E+05	1.81E+04	0.2674	722	880	503.26	524
Isoprene	9.54	0.24	2.51E+06	9.13E+04	0.2999	869	919	510.54	520
Methane, iodo-	10.18	0.29	4.73E+05	1.48E+04	0.1667	852	940	526.87	530
Methylene chloride	10.55	0.33	6.02E+06	2.39E+05	0.3335	919	924	536.18	531
Pentane, 3-methyl-	12.37	0.20	2.89E+05	1.12E+04	0.2333	696	848	582.64	580
n-Hexane	13.08	0.19	8.04E+05	3.34E+04	0.2003	857	906	600	600
2-Butanone	13.14	0.92	1.06E+06	1.67E+04	0.2332	545	845	601.87	602
Cyclopentane, methyl-	14.58	0.21	4.26E+05	1.65E+04	0.167	786	906	633.74	629
Tetrahydrofuran	14.69	0.51	1.44E+05	3.93E+03	0.2319	559	921	636.18	621
Benzene	16.24	0.35	6.60E+05	3.03E+04	0.2338	881	915	670.34	662
Pentanal	18.23	0.63	3306.726	1.41E+03	0.0667	557	826	714.78	696

1,4-Dioxane	18.30	0.56	1.27E+05	5.01E+03	0.1333	688	808	716.27	670
Toluene	21.02	0.32	7.79E+05	2.99E+04	0.2003	868	896	778.09	769
Octane	22.01	0.15	3.09E+05	1.20E+04	0.2339	747	842	800	800
Hexanal	22.15	0.65	1.09E+05	4.38E+03	0.1665	675	862	804.20	802
m-Xylene	25.38	0.27	3.87E+05	1.13E+04	0.1668	572	920	883.51	872.5
Nonane	26.08	0.13	4.56E+05	1.52E+04	0.1673	790	852	900	900
o-Xylene	26.42	0.30	65231.01	3.37E+03	0.1333	618	764	909.98	908
α-Pinene	28.06	0.18	2.07E+05	1.06E+04	0.1337	725	790	953.55	940
Camphene	28.79	0.21	2.21E+05	6.93E+03	0.2656	755	835	973.05	951
Octanal	30.14	0.53	6.01E+05	1.36E+04	0.3998	791	893	1009.65	1005
Benzene, 1,4-dichloro-	31.21	0.33	54936	2.89E+03	0.1999	581	634	1040.64	1021.24
Benzene, 4-ethyl-1,2-dimethyl-	31.32	0.20	1.48E+05	4.30E+03	0.1998	536	597	1043.89	1026
Undecane	33.29	0.09	3.28E+05	1.61E+04	0.1669	745	843	1100	1100
Nonanal	33.67	0.49	7.36E+05	2.15E+04	0.2332	781	825	1112.77	1102
Decanal	37.09	0.44	1.49E+05	4.43E+03	0.1998	666	743	1219.57	1200
Naphthalene-D8	37.46	0.38	1.22E+06	2.23E+04	0.433	775	891		

$^{1}t_{r}$ – First dimension retention time, $^{2}t_{r}$ – Second retention time, RI – Retention index, Lit. RI – Literature Retention Index

Looking at the two samples, there is some overlap in the analytes since in both Figure 3.3 and Figure 3.5 which include the alkanes, aldehydes, xylenes, acetone, and ethanol. Several of these are not among the target analytes that EPA methods report. This overlap between the two samples can be linked to the fact that both locations had fuel combustion taking place which can introduce compounds such as the alkanes and xylenes.[164,171] Table 3.2 gives a more detailed list of the analytes present in the air sample to get an insight of the VOCs present with names determined though mass spectral library searching, and RI values included for better identification. Looking at the match factors, only two analytes showed low values, hexanal and 4-ethyl-1,2-dimethylbenzene, which indicates that these compounds could be misidentified by the library search. The rest of the analytes showed good match factor values as these were above 700. RI values for the majority of the analytes present are within close margin to their literature values with differences between ten or twenty, while other compounds such as 1,4-dichlorobenzene, 4-ethyl-1,2,-dimethyl-benzene, 1,4-dioxane, and pentanal showing larger differences. This difference between the RI values and mass spectral library search results could be a result of the low responses, seen by the areas, which can lead to poor library matches. Table 3.2 gives the internal standard an area of 1.22×10^{6} which is comparable to the values seen in the individual internal standard runs. Based on this observation, it can be stated there is no sample loss in this sorbent tube sample that occurred during sampling. It is important to say the leak does make it difficult to determine if there is any sample loss.

Looking at the target compounds present at the University of Alberta Construction; it was measured that tetrahydrofuran was present in the air at concentration of 0.21 ppbv. Another target VOC seen in this sample was o-xylene which was present in the air at a concentration of 0.11 ppbv. Like the previous sampling site, the University of Alberta Bus Station, these VOCs were at concentrations below the EPA range which allows for measurement at lower levels. However, the leak also impacted the results as some analytes was lost during the analysis which leads to discrepancies in the measurements. Therefore, these values are likely not representative of the actual concentrations at the site.

The presence of α-pinene, a type of biogenic VOC, is linked to the trees present above the sampling pumps and sorbent tubes as this terpene has been found before when sampling forest locations or in wood constructions.[173,174] Other biogenic VOCs found in this sample were isoprene and camphene which is can be found in forest locations similar to α-pinene.[175,176] The trees and other plants near the sampling site can contribute these biogenic compounds to the atmosphere and these may impact ozone formation. Looking at other works with non-industrial locations, compounds such as various alkanes, xylenes, methylene chloride, and α-pinene can be expected in non-industrial locations such as a university.[177] Periodically construction vehicles or trucks were used near the sampling location and the exhaust from these vehicles could introduce the xylenes and alkanes into the air .[171] Gasoline can introduce the alkanes as well as various aromatic compounds which was seen in Table 3.1 and Table 3.2 which makes sense as in both cases vehicles using gasoline were near.[178] The presence of the construction vehicles and trucks is likely the source of the xylenes as well as the straight chain and branched alkanes. However, the presence of these vehicles was not constant which could explain why the xylenes had lower responses and the absence of ethylbenzene compared to the University of Alberta Bus Station sample. However, the ethanol found in the sample could be related the burning of the fuel in the construction vehicles.[1]

3.3.1.3 Goldbar Park Parking Lot Construction Site

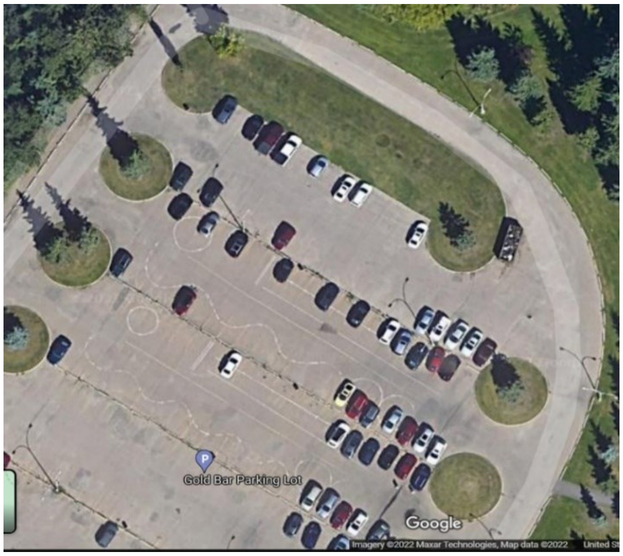
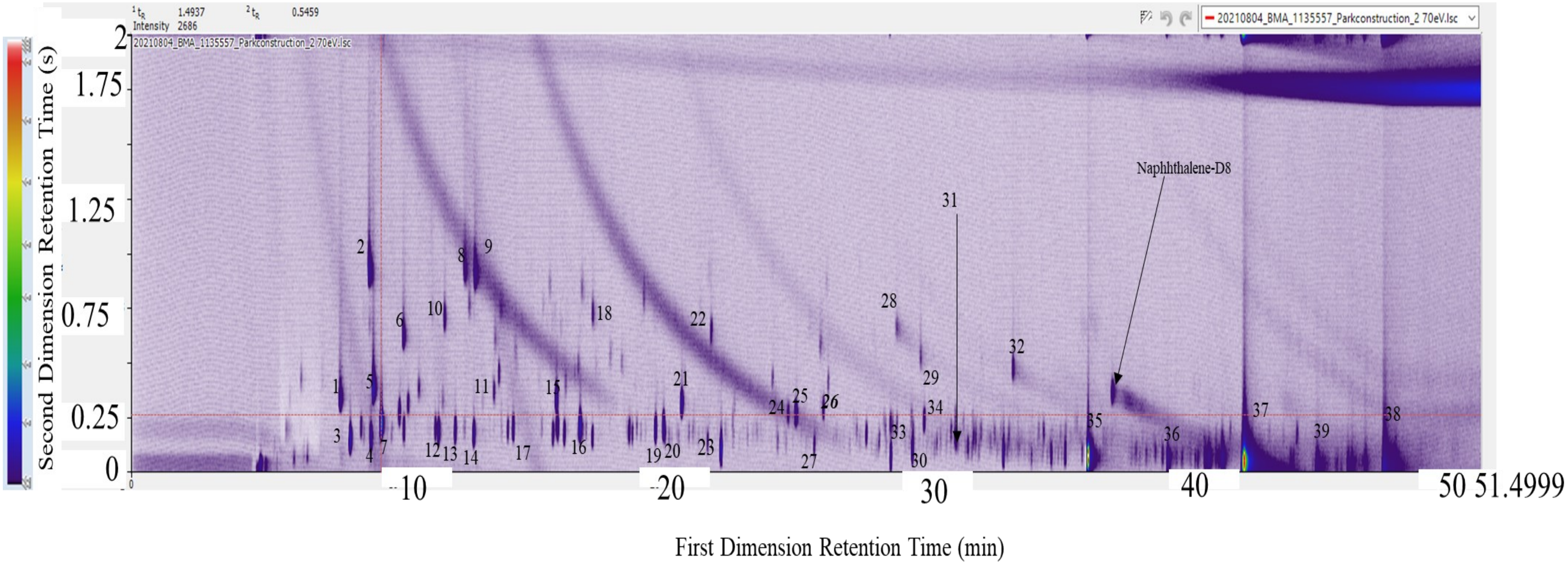


Figure 3.6: Image of the Goldbar Park Parking Lot Sampling Site - Image from Google Maps[179]

Another site sampled was a public park in Edmonton AB, Goldbar Park, more specifically the parking lot due to construction taking place there. Figure 3.6 gives an image of the Goldbar Park parking lot from Google Maps, and it is important to note that the construction took place in the upper part of the parking lot.[179] The sampling took place in the summer on August 4, 2021, from 3:46 pm to 4:46 pm and the temperature was 29.2 ℃ at 4 pm according to the Government of Canada's data.[180] The sampling pumps were calibrated to collect at a rate of 50.56 mL/min for 60 minute giving a sample volume of 3.03 L. Here the sampling pumps were set up close to the construction activity then the air was sampling for one hour. The sampling pumps and sorbent tubes were placed on top of Dr. Harynuk's vehicle which was parked very close to the construction.

At this sampling site, there were three potential sources of VOCs: vehicle exhaust from cars, the construction activity, and biogenic sources. The biogenic sources present were the trees and other types of vegetation present along the outside of the parking. As a result of these sources, it can be expected that aromatic compounds would be present due to the gasoline use and biogenic compounds can also be expected.[1] The fact that there are two sources of fuel exhaust compounds presents larger chance that aromatic compounds will be present in the air at this site.[1] Figure 3.7 shows the GC×GC-TOFMS results for the 60-minute air sample collected at this site and the most abundant VOCs detected in the sample are labeled below the chromatogram.



1. Ethanol
2. Acetone
3. Butane,2-methyl
4. Pentane
5. Isopropyl Alcohol
6. Acetic Acid Methyl Ester
7. Isoprene
8. Methyl Vinyl Ketone
9. 2-butanone
10. Methacrolein
11. Furan, 2-methyl
12. Pentane, 2-methyl
13. Pentane, 3-methyl
14. Hexane*
15. Benzene*
16. Pentane, 2,2,4-trimethyl
17. Methylcyclopentane
18. Pentanal
19. Pentane, 2,3,4-trimethyl
20. Pentane, 2,3,3-trimethyl
21. Toluene*
22. Hexanal
23. Octane
24. Ethylbenzene
25. m-xylene
26. o-xylene
27. Nonane
28. Benzaldehyde
29. Octanal
30. Decane
31. Limonene
32. Nonanal
33. Benzene, 1-ethyl-3-methyl
34. Benzene, 1,2,4-trimethyl
35. Dodecane
36. Tridecane
37. Tetradecane
38. Hexadecane
39. Pentadecane

*- Known Artifacts Compounds

Figure 3.7: GC×GC-TOFMS Chromatogram of an Air Sample Collected at Goldbar Park near Parking Lot Construction in Edmonton, AB

Table 3.3: Goldbar Park Parking Lot Construction Site Total Ion Chromatogram Data from TOFMS Results

Compound Name	^1t_r (min)	^2t_r (s)	Area	Height	Width	Similarity	Reverse	RI	Lit. RI
Ethanol	7.95	0.32	1.70E+06	4.07E+04	0.3668	857	934		
Butane, 2-methyl-	8.35	0.15	2.65E+06	1.21E+05	0.2671	903	916		
Acetone	9.05	0.91	3.14E+06	6.59E+04	0.4325	909	913		
Pentane	9.13	0.15	1.72E+06	6.72E+04	0.2666	851	903	500	500
Isopropyl Alcohol	9.22	0.37	3.24E+06	1.03E+05	0.3335	936	960	502.26	524
Isoprene	9.52	0.22	5.80E+06	2.66E+05	0.3002	925	934	510.04	520
Acetic acid, methyl ester	10.37	0.62	1.27E+06	3.50E+04	0.2663	851	887	531.73	531
Butane, 2,2-dimethyl-	10.38	0.19	5.25E+05	1.87E+04	0.2003	774	866	531.99	526.3
Methylene chloride	10.57	0.32	2.30E+05	1.21E+04	0.1332	735	911	536.62	531
Butane, 2,3-dimethyl-	11.59	0.20	3.95E+05	2.04E+04	0.1335	783	843	562.75	557.9
Pentane, 2-methyl-	11.72	0.18	1.34E+06	4.71E+04	0.233	887	934	565.88	559
Methacrolein	11.94	0.70	7.51E+05	1.96E+04	0.3997	782	868	571.73	566
Pentane, 3-methyl-	12.35	0.19	8.93E+05	3.56E+04	0.2003	823	870	582.03	580
Methyl vinyl ketone	12.77	0.92	9.93E+05	2.03E+04	0.2333	747	878	592.62	606
n-Hexane	13.06	0.17	1.32E+06	5.59E+04	0.2670	893	930	600	600
2-Butanone	13.11	0.90	2.36E+06	4.30E+04	0.2996	763	875	601.14	602

Furan, 2-methyl-	13.82	0.37	2.68E+05	1.18E+04	0.1334	733	804	616.94	604
Pentane, 2,4-dimethyl-	14.36	0.19	3.78E+05	1.50E+04	0.2003	737	816	628.74	621
Cyclopentane, methyl-	14.56	0.20	7.57E+05	3.32E+04	0.2003	848	915	633.15	629
Hexane, 2-methyl-	16.08	0.17	5.68E+05	2.37E+04	0.2007	830	875	666.80	659
Benzene	16.21	0.33	1.56E+06	6.48E+04	0.3335	899	917	669.73	662
Carbon Tetrachloride	16.22	0.21	3.58E+05	2.55E+04	0.1000	711	968	669.94	663
Pentane, 2,3-dimethyl-	16.26	0.20	4.21E+05	2.89E+04	0.1335	641	852	670.87	675.8
Hexane, 3-methyl-	16.51	0.17	6.33E+05	2.75E+04	0.1670	847	898	676.33	667
Butane, 2,2,3,3-tetramethyl-	17.12	0.21	2.91E+06	1.19E+05	0.2001	875	900	689.68	720
Heptane	17.58	0.16	4.29E+05	1.78E+04	0.1670	799	851	700.00	700
Pentanal	17.59	0.72	5.58E+05	1.30E+04	0.3336	743	849	700.20	696
Hexane, 2,4-dimethyl-	19.11	0.17	3.25E+05	1.14E+04	0.2003	792	855	734.64	736
Pentane, 2,3,4-trimethyl-	19.99	0.19	1.33E+06	5.81E+04	0.2003	875	893	754.75	759
Pentane, 2,3,3-trimethyl-	20.29	0.21	1.65E+06	6.11E+04	0.2331	839	866	761.62	768
Toluene	20.99	0.31	2.00E+06	7.96E+04	0.2999	911	931	777.42	769
Octane	21.98	0.14	3.28E+05	1.12E+04	0.1670	729	856	800	800
Hexanal	22.14	0.64	1.15E+05	1.02E+04	0.0999	763	896	803.99	802
p-Xylene	25.35	0.26	1.20E+06	3.77E+04	0.2000	763	915	882.80	860
Nonane	26.05	0.12	3.95E+05	1.27E+04	0.1672	742	844	900	900

o-Xylene	26.41	0.29	4.26E+05	1.45E+04	0.1669	826	903	909.65	908
α-Pinene	28.04	0.17	4.03E+05	1.88E+04	0.1335	794	847	952.99	940
Benzene, 1-ethyl-4-methyl-	28.96	0.22	2.64E+05	1.26E+04	0.1332	739	874	977.34	965.3
Benzene, 1,2,4-trimethyl-	29.19	0.21	2.13E+05	7.72E+03	0.2007	732	818	983.61	976
Decane	29.81	0.10	1.14E+06	5.20E+04	0.1668	884	914	1000	1000
Benzene, 1-methyl-3-(1-methylethyl)-	31.27	0.19	2.83E+05	1.00E+04	0.1337	720	813	1042.46	1030
Limonene	31.48	0.14	2.69E+05	1.43E+04	0.1000	730	854	1048.42	1031
Undecane	33.26	0.08	1.27E+06	5.46E+04	0.1672	840	877	1100	1100
Nonanal	33.64	0.47	6.21E+05	1.86E+04	0.2670	782	814	1111.81	1102
Dodecane	36.49	0.07	2.85E+07	1.24E+06	0.4336	893	913	1200	1200
Naphthalene-D8	37.42	0.36	1.02E+06	2.50E+04	0.3666	798	889		
Tridecane	39.54	0.06	2.17E+06	5.75E+04	0.4004	845	894	1300	1300
Tridecane, 3-methyl-	41.68	0.06	1.79E+06	5.59E+04	0.2335	779	836	1373.49	1371
Tetradecane	42.45	0.04	6.68E+07	1.19E+06	1.1331	901	922	1400	1400
Pentadecane	45.23	0.03	1.19E+06	2.70E+04	0.2001	798	903	1500	1500
Hexadecane	47.79	0.02	4.61E+06	7.71E+04	0.3001	706	812	1600	1600

$^{1}t_r$ – First dimension retention time, $^{2}t_r$ – Second retention time, RI – Retention index, Lit. RI – Literature Retention Index

An expanded list of the VOCs present in the Goldbar Park parking lot is given in Table 3.3 with a larger number of compounds detected compared to the previous samples. In terms of potential loss during the sampling process, the naphthalene-D8 response level is comparable to initial internal standard runs. This indicates that there is no loss of analytes due to the sampling conditions which is the goal for sampling parameters. The match factors for these analytes were greater than 700 except for 2,3-dimethylpentane meaning this could be a different isomer resulting in the lower similarity value. The VOCs found in this sample had differences of RI values between ten and twenty when compared to known values. These reasonable differences between the sample and known RI values indicates that the compound identities determined by the mass spectral library are likely correct. Looking at both Figure 3.7 and Table 3.3, most of the VOCs present are not a part of the target compound list.

Examination of the target VOCs present in the Goldbar Park Construction site sample showed that there were few target compounds present in the calibration range. Looking at the concentration of o-xylene present in the air at this site, it measured to be at 0.13 ppbv using this method. Another target VOC, 1,2,4-trimethylbenzene was measured to be 0.09 ppbv in the air at the site. These measurements were below the EPA range and therefore this method gives the ability to analyze compounds at levels below the EPA range. As with the other outdoor samples, the leak discovered after the work was completed lead to the variations in the analyte responses as well as variations in concentrations of the analytes. As a result of the leak, the concentrations determined here are likely not representative of the actual concentrations at that sampling location.

There is a significant increase in the number of alkanes present compared to previous outdoor samples which is similar to urban locations despite the site being a park which could be related to the construction.[142,181] The construction and the cars traveling through the parking lot both contribute to the increase in alkanes similar to what might be seen on roadsides.[181] The exhaust of the various vehicles present, both construction and normal vehicles, has led to the high responses of alkanes ranging up to hexadecane.[171] α-pinene was also found this sample and it has been seen in other works in urban samples but being a biogenic VOC, it can also be connected to the forest nearby since this VOC has been linked to wood.[174,181] The presence of the biogenic VOCs, isoprene and limonene, is likely linked to the nearby forest producing terpene compounds.[176,182] While these are naturally occurring, these compounds can lead to the production of other pollutants such as ozone.[11] Ozone itself is a health risk at the ground level and as a result the presence of biogenic VOCs should still be monitored due to the production of other pollutants. Of the outdoor samples shown so far, the Goldbar Park sample had the greatest number of compounds which can be connected to high level of activity at the park on that day.

3.3.1.4 Outdoor Sampling Site Summary

Seven outdoor sampling sites were examined in this work ranging from public parks to busy roadsides which provided a diverse set of samples. Common sources at these sites were fuel combustion in vehicles and biogenic sources such forests. In Figure 3.8, the most abundant compounds at the seven sites sampled are featured to summarize the VOCs found across the different sites. The compounds were divided into classes to see how many VOCs from each class were present in the samples.

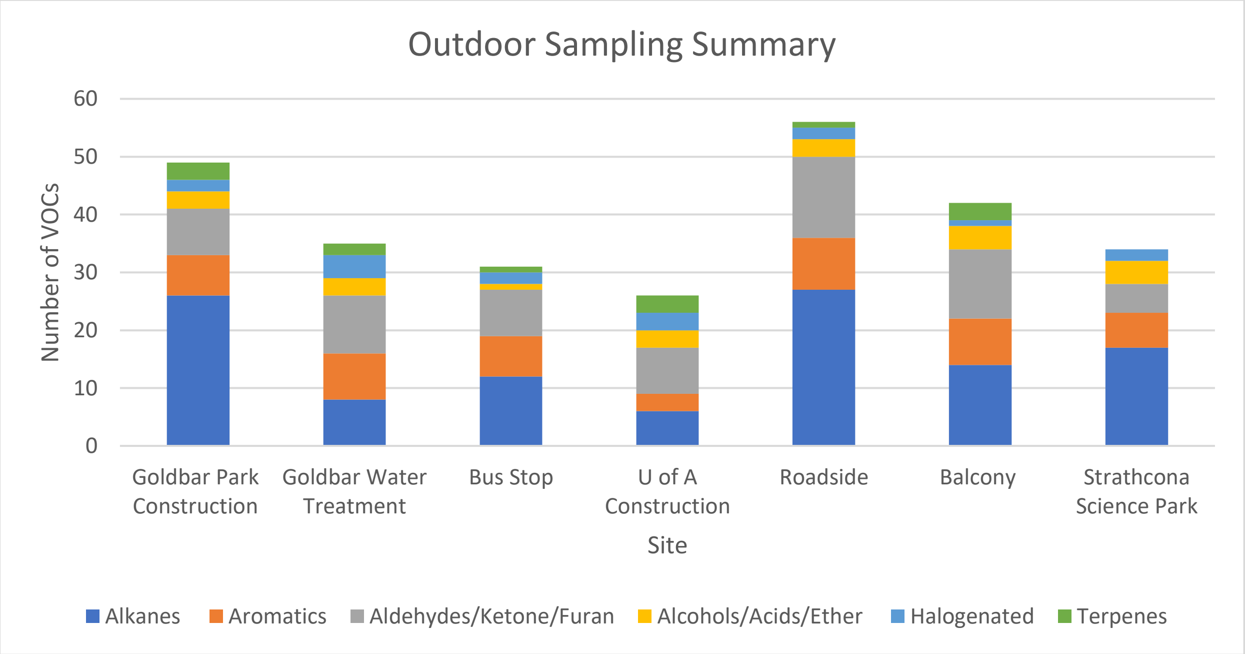
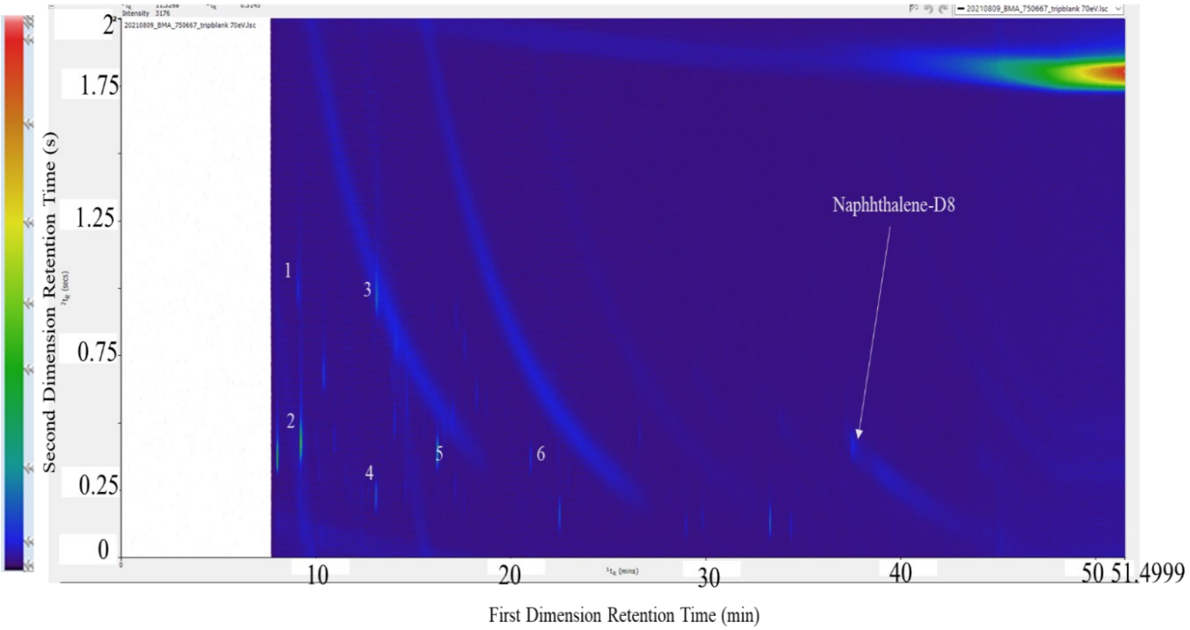


Figure 3.8: Summary of the Most Abundant VOCs Present in the Outdoor Air Samples

At many of these sites, the alkanes (both straight chain and branched) are the most significant part of the sampling medium. Looking at the overall number of significant compounds, the University of Alberta construction site seems to have a lower number of VOCs. This could be related to location of the sampling pumps related to the construction itself. While there were vehicles that occasionally went by the sampling location, there was little activity near the sampling devices. Furthermore, it is possible that the wind conditions swept the VOCs to the south while the sampling set up was in the opposite direction. Locations with the larger number of VOCs were the Goldbar Park construction site and roadside location which was near 34th Street outside of Edmonton, AB. The common factor between the two locations is the proximity to sources of VOCs as other sampling set ups were placed further from the sources. Both urban sites and roadsides have been studied in the literature with the many of the alkanes seen in this work ranging from isobutane to undecane matching what was seen in previous works.[181] Both in the roadside sample and the Goldbar Park sample there are many alkanes as well as several aromatic compounds such as xylenes.[181] The alkanes were being present at all of the sampling sites is likely connected to the various sources of fuel or vehicle exhaust.[171] Aromatic compounds are the next most abundant compounds in most of the sampling sites. The presence of aromatic compounds can be connected to vehicle emissions or other industrial emissions at the sampling sites.[77] These along with the alkanes are expected at these locations as a result of the sources present. Terpenes were found in nearly all of the outdoor samples and these can be introduced by trees as well as other types of vegetation.[173]

Aldehydes found in the samples can be found in the atmosphere as a result biogenic emissions from nearby forests or nonurban locations, particularly for less volatile aldehydes.[183,184] These VOCs can undergo photolysis and contribute to the production of other pollutants in the atmosphere.[185] However, it is important to note that biogenic sources, despite being a major emission source, are not the only source of these oxygenated VOCs as they can be produced by vehicle emissions.[184] Few halogenated compounds where seen in these samples and one of these was methylene chloride. This is a common solvent and it may have been present if any metal cleaning or degreasing was taking place in the area.[29] It is possible that these activities may have construction sites sampled at as methylene chloride was seen in these samples. There is overlap between the different sampling sites which is related to the similarities between them. Several of these were near vehicle emissions which are a well-known source of VOCs and prolonged exposure may be a risk for some individuals.



1. Acetone
2. Isopropyl Alcohol
3. 2-butanone
4. Hexane*
5. Benzene*
6. Toluene*

*- Known Artifacts Compounds

Figure 3.9: GC×GC-TOFMS Chromatogram of a Capped Universal Sorbent Used as Trip Blank

At for every sampling site, a sealed sorbent tube wrapped in aluminum foil which remained unopened in the transport container was used as trip blank for each sampling trip. The purpose of this was to account for any compounds which could have entered the sorbent tube during travel and storage of the sorbent tubes to or from the sampling sites. A solvent delay was used as since these sorbent tubes were not used for sampling, therefore there would be increased amount of methanol due to the lack of sampling flow which could harm the filament in the TOFMS. An example of these is seen in Figure 3.9 and each of the other chromatograms of the other trip blanks showed similar profiles. This indicates that there were minimal VOCs present from transport and a couple of the compounds found were artifacts from the sorbent (hexane, benzene, and toluene). For the other compounds, the responses are not high except for isopropyl alcohol having an area of $2.45\times 10^6$and the isopropyl alcohol could have been introduced during the preparation for sampling. Therefore, other than the compounds seen her, all compounds found in the sampled sorbent tube are related to the sampling sites not the travel.

3.3.2 Indoor Air Samples

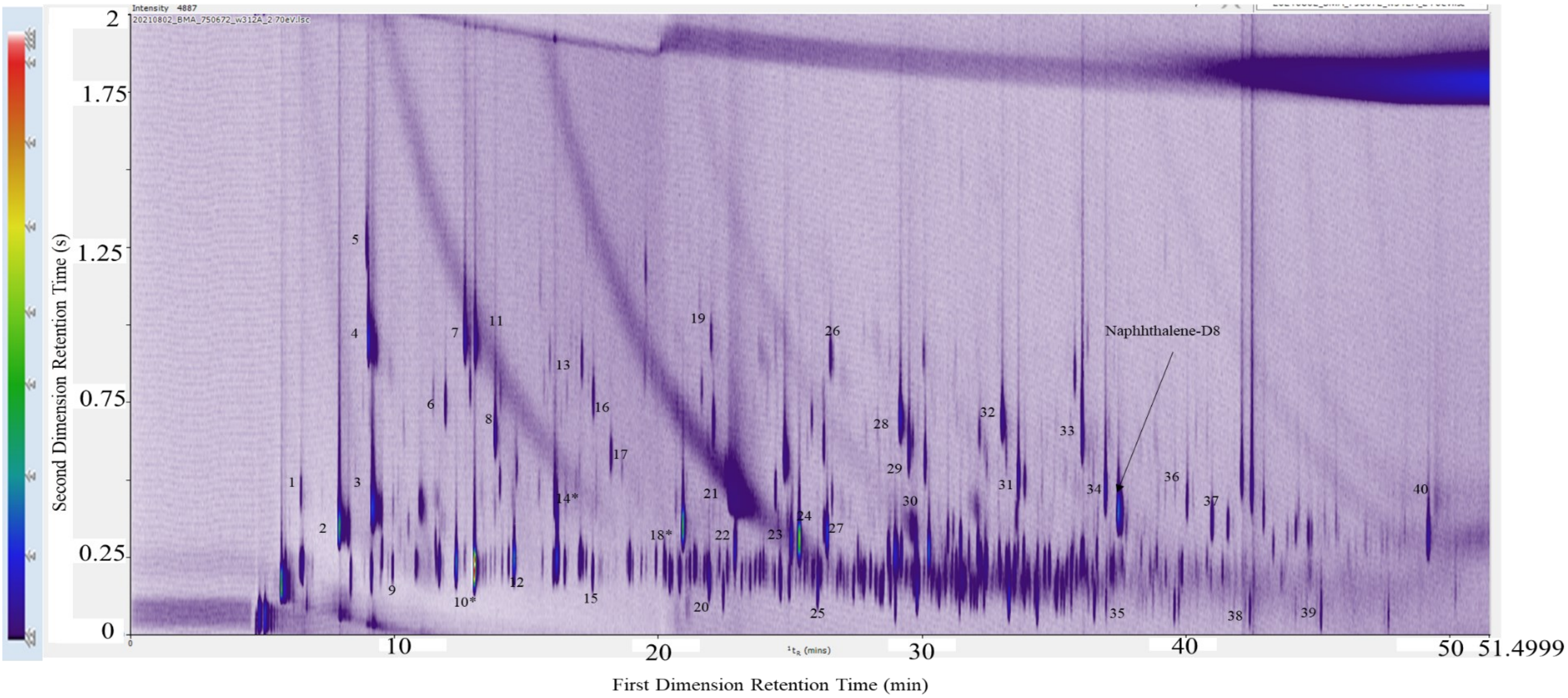
Indoor locations for workplace monitoring were various laboratory spaces in the University of Alberta Chemistry Department and public space in the University of Alberta's Medical Science Building. Supervisors of each location gave permission for the space to be sampled prior to sampling taking place. These locations had the potential to have VOCs such as solvents or other general laboratory chemicals present. After loading the internal standard, the sorbent tubes were tightly capped with brass caps then wrapped in aluminum foil and placed in a plastic container for transport. A trip blank was included with the sorbent tubes to account for any VOCs which entered the sorbent during transit not sampling. Each site had duplicate samples collected using the same conditions for sampling though flow rate may have been slightly different.

An internal standard of naphthalene-D8 was used to determine any loss that occurred during sampling. Naphthalene-D8 was selected as it does not naturally occur in the atmosphere. The concentration was selected to be in the range of the compounds of interest to avoid impacting the response of nearby analytes. Therefore, the concentration of the internal standard was 4.21 mg/L and three replicates of 1.0 μL of solution spiked onto sorbent tubes. These sorbent tubes were analyzed prior to any sampling taking place and the areas were 1.11×10^6, $1.04 \times 10^6$and 5.98×10^5. Based on these results, any areas less than these values would indicate that there was loss of internal standard during sampling. It is critical to state that these values may have impacted by the leak. As a result, any determination in sampling loss may not be completely accurate due to the variations in these responses. When sampling was complete, the caps were resealed on both ends of the sorbent tube then the aluminum foil was wrapped around the sampler before placing the sampler in back in the container. Sampled sorbent tubes were analyzed upon returning to the laboratory after all sampling was completed for that day. Compound identifications were based on mass spectral library searching the data files from the 70 eV results with retention index values included as well. Calculated RI values were compared to literature RI values from NIST databases or PubChem.

As stated with the outdoor air samples, the leak discovered after the samples were analyzed significantly impacts the ability to effectively quantify the VOCs present in the samples. It is highly likely that the concentrations present at the sampling site were higher than what the responses from analysis showed. The presence of the leak leads to the risk of VOCs being falsely determined to be at a safe level when they are present at higher concentrations. Therefore, any quantification results can not be seen as completely accurate due to the leak causing the results to be underrepresented. Also, sample loss can not be accurate determined as the leak could have led to lower values as a result of loss during the analysis not sampling.

3.3.2.1 Harynuk Chemical Storage

One of the indoor locations sampled for workplace air quality monitoring was a chemical storage room in the Department of Chemistry which had four chemical storage cabinets and three refrigerated storage units. The storage room was used by the Harynuk Research Group for storing chemicals in both room temperature storage cabinets and refrigerated locations. One the day of the sampling, the activity in the room was minimal and as a result the responses are not from any experiments taking place. This sample was collected on August 2, 2021, from 3:39 pm to 4:39 pm on the bench in the storage room. The sampling pump was calibrated to collect at a rate of 50.45 mL/min for 60 minutes giving a sample volume of 3.03 L. Here it was expected that there would be a variety of VOCs present due to the storage of chemicals in the space. This includes common solvents such as acetone and hexane which are stored in one of the cabinets. The other chemical storage cabinets held a wide range of the chemicals, and these could potentially be released into the room air. Many of the storage cabinets have vents attached to them, however, at least one did not which could release some VOCs into the air. The compounds listed below the chromatogram in Figure 3.10 are some of the most abundant VOCs found in the air in the chemical storage room. Table 3.4 gives an extended list of the VOCs present in the sample collected at this location. The color bar on the left side of the chromatogram in Figure 3.10 represents the intensity of the peaks present in the sample.



1. Acetaldehyde
2. Ethanol
3. Isopropyl Alcohol
4. Acetone
5. Butanenitrile
6. Methacrolein
7. Methyl Vinyl Ketone
8. Ethyl Acetate
9. Carbon Disulfide
10. Hexane*
11. 2-Butanone
12. Cyclopentane, methyl
13. 2-pentanone
14. Benzene*
15. Heptane
16. Pentanal
17. 1,4-dioxane
18. Toluene*
19. Cyclopentanone
20. Octane
21. Pyridine
22. Tetrachloroethylene
23. Ethylbenzene
24. m-xylene
25. Nonane
26. Cyclohexanone
27. o-xylene
28. Benzaldehyde
29. Octanal
30. Benzene, 1,2,4-trimethyl
31. Nonanal
32. Acetophenone
33. Diethylfumerate
34. Decanal
35. Tridecane
36. Undecanal
37. Naphthalene, 1-methyl
38. Tetradecane
39. Pentadecane
40. Diphenyl sulfide

*- Known Artifacts Compounds

Figure 3.10: GC×GC-TOFMS Chromatogram of a Harynuk Laboratory Chemical Storage Room

Table 3.4: Total Ion Chromatogram Data from TOFMS Results from Air Sampling Collected in the Harynuk Chemical Storage Room

Compound Name	^1t_r (min)	^2t_r (s)	Area	Height	Width	Similarity	Reverse	RI	Lit. RI
Acetaldehyde	6.45	0.46	4.02E+05	15229.56	0.2329	857	932		
Ethanol	7.91	0.35	1.30E+07	5.72E+05	0.4000	938	938		
Butanenitrile	8.93	1.24	5.68E+05	22993.26	0.1661	774	849		
Acetone	9.01	0.95	5.11E+06	1.99E+05	0.2665	916	921		
Isopropyl Alcohol	9.15	0.41	9.00E+06	2.37E+05	0.3333	954	964	500.52	524
Isoprene	9.52	0.26	3.38E+05	16360.39	0.1336	774	876	509.90	520
Carbon disulfide	10.81	0.23	6.05E+05	17397.75	0.2334	842	886	542.88	544
Pentane, 2-methyl-	11.69	0.23	1.45E+06	70702.87	0.2003	895	942	565.28	559
Methacrolein	11.92	0.74	6.95E+05	25517.75	0.2000	837	888	571.19	566
Pentane, 3-methyl-	12.33	0.23	5.36E+06	2.92E+05	0.2337	913	918	581.41	580
Methyl vinyl ketone	12.65	0.95	3.53E+06	88180.79	0.3666	891	945	589.77	606
n-Hexane	13.02	0.22	2.73E+07	1.28E+06	0.2337	940	944	600.0	600
2-Butanone	13.05	0.94	3.04E+06	76294.9	0.3332	844	918	599.93	602
Furan, 3-methyl-	13.79	0.41	1.05E+05	4232.711	0.1998	634	705	616.22	611.1
Ethyl Acetate	13.81	0.64	1.83E+06	77968.39	0.2666	879	889	616.70	618
Pentane, 2,4-dimethyl-	14.32	0.24	3.47E+05	14727.51	0.1671	752	798	627.85	621

Cyclopentane, methyl-	14.52	0.24	5.28E+06	2.53E+05	0.2669	914	932	632.32	629
Hexane, 2-methyl-	15.99	0.21	2.83E+05	22060.07	0.1002	804	842	664.86	659
Cyclohexane	16.14	0.24	4.85E+06	2.29E+05	0.1669	912	920	668.23	687.4
Benzene	16.15	0.38	1.82E+06	77296.39	0.1669	878	917	668.39	662
Pentane, 2,3-dimethyl-	16.24	0.25	2.84E+05	26534.36	0.1000	773	856	670.31	675.8
Hexane, 3-methyl-	16.45	0.22	5.77E+05	27536.87	0.1670	805	856	674.90	667
Pentane, 2,2,4-trimethyl-	17.04	0.25	9.57E+05	37622.05	0.1669	792	803	687.94	680
2-Pentanone	17.09	0.88	3.70E+05	14573.37	0.1670	734	802	689.09	687
Heptane	17.51	0.20	6.68E+05	36993.96	0.1336	859	889	700	700
Cyclohexane, methyl-	18.91	0.24	7.03E+05	32040.04	0.1337	795	860	730.17	713
Heptane, 2-methyl-	20.42	0.19	8.40E+05	34118.29	0.2000	803	849	764.52	763
Heptane, 4-methyl-	20.54	0.20	1.59E+05	12306.28	0.1001	660	744	767.25	764
Heptane, 3-methyl-	20.79	0.19	7.51E+05	32430.5	0.2333	805	846	772.99	770
Toluene	20.92	0.35	1.12E+07	5.85E+05	0.2003	922	922	775.92	769
Heptane, 2,2-dimethyl-	21.19	0.22	2.88E+05	12761.33	0.1335	702	741	782.02	816
Octane	21.92	0.18	1.91E+06	81774.82	0.1669	837	905	800	800
Cyclopentanone	21.99	0.96	3.09E+05	10734.19	0.1664	717	844	800.31	797

Hexanal	22.08	0.68	9.52E+05	30781.6	0.2001	831	937	802.38	802
Pyridine	22.69	0.45	1.48E+06	25810.96	0.1992	655	886	817.34	747
Tetrachloroethylene	22.89	0.27	2.67E+06	1.24E+05	0.2006	923	976	822.33	815.15
Ethylbenzene	25.02	0.30	3.37E+06	1.35E+05	0.2667	872	922	874.73	864.1
m-Xylene	25.32	0.31	1.49E+07	6.56E+05	0.2999	917	945	882.07	872.5
Nonane	26.03	0.16	2.03E+06	91707.26	0.1670	839	925	900	900
Styrene	26.28	0.35	4.14E+05	16452.8	0.1334	823	914	906.09	882
o-Xylene	26.38	0.33	4.95E+06	2.03E+05	0.2003	916	940	908.89	908
Cyclohexanone	26.51	0.90	6.85E+05	18433.48	0.2330	779	809	912.36	895
Octane, 2,6-dimethyl-	27.39	0.17	5.81E+05	24340.1	0.1672	815	878	935.72	935.12
Nonane, 4-methyl-	28.40	0.15	6.11E+05	20742.22	0.1667	784	861	962.47	962
Nonane, 2-methyl-	28.50	0.16	6.77E+05	24538.51	0.1673	790	827	965.31	964
Benzene, propyl-	28.71	0.27	1.20E+06	43301.83	0.1998	866	902	970.85	962
Benzaldehyde	29.15	0.70	3.94E+06	1.17E+05	0.3994	921	933	982.64	972
Benzene, 1,2,4-trimethyl-	29.19	0.25	1.79E+06	72130.31	0.2005	886	908	983.68	976
Phenol	29.62	0.35	7.61E+05	13978.05	0.2997	738	935	994.95	992
Benzene, 1-ethyl-2-methyl-	29.73	0.28	8.39E+05	50474.08	0.0998	840	879	997.96	971
Decane	29.80	0.14	2.36E+06	1.16E+05	0.1338	884	921	1000	1000

Octanal	30.09	0.56	9.79E+05	36509.54	0.3330	865	926	1008.29	1005
Benzene, 1,3-dichloro-	31.18	0.34	1.24E+05	6937.579	0.1669	702	851	1039.65	1022
p-Cymene	31.28	0.20	7.31E+05	22933.83	0.1335	676	710	1042.65	1026
Acetophenone	33.02	0.70	2.10E+06	56185.9	0.2331	848	887	1093.02	1078
Nonanal	33.64	0.51	2.17E+06	92089.35	0.2003	884	897	1111.7	1102
Naphthalene-D8	37.42	0.40	8.87E+06	3.30E+05	0.3998	862	902		
Tridecane	39.53	0.09	2.05E+05	16421.54	0.1002	745	817	1300	1300
Naphthalene, 1-methyl-	40.97	0.37	1.09E+06	42598.39	0.2337	851	904	1349.20	1325
Tetradecane	42.40	0.08	4.35E+05	16755.76	0.1335	745	850	1400	1400
Pentadecane	45.10	0.07	4.74E+05	18266.76	0.1336	786	897	1500	1500

^1t_r – First dimension retention time, ^2t_r – Second retention time, RI – Retention index, Lit. RI – Literature Retention Index

Regarding potential sampling loss, the response from naphthalene-D8 is 8.87×10^6 which when compared to the results from initial internal standard runs indicates that there is no sample loss. However, the response is higher than seen in the initial runs despite similar amount being applied to the sorbent tubes. As mentioned, the compound names were determined using the library searching and the retention indices were included for improved identification. With respect to the match factors, all but two analytes have match factors above 700, these two being 4-methylheptane and p-cymene, which indicates good matches for most of the VOCs. Most of the VOCs found in the chemical storage room had RI values close to known values, however there were some compounds which had larger differences from the known values. Compounds such as pyridine and 2,2-dimethyl-heptane have larger differences for the retention indices which leads to uncertainty in the compound's identity. The identities of the other VOCs with closer calculated values are the ones determined by the mass spectral library.

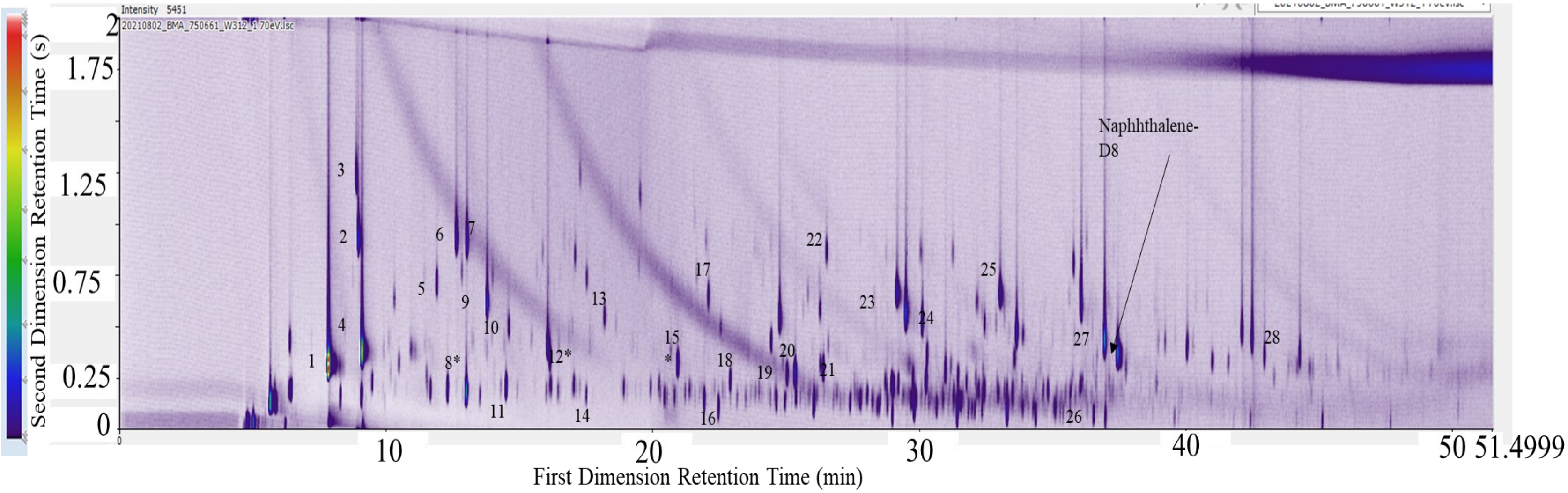
Just as with the outdoor samples, the target VOCs can be quantified using the thermal desorption calibrations performed in Chapter 2 as long as they were in that calibration range. One of the compounds seen in the chemical storage room was ethylbenzene which was present in the air at a concentration 0.30 ppbv. o-Xylene and propylbenzene were present in the air at higher levels, both at 0.45 ppbv in the air. Other aromatic hydrocarbons, styrene and 1,2,4-trimethylbenzene were present in the air at concentrations of 0.17 ppbv and 0.09 ppbv respectively. Like the outdoor samples, these VOCs were at levels below the EPA range. It should be stated that the leak resulted in response variations at this site as well. This means that the concentrations found here are likely not truly representative of the concentrations at the sampling site.

One of the compounds found was isopropyl alcohol which was used in the space for cleaning as well as in hand sanitizer. The presence of the containers with isopropyl alcohol in the laboratory space near the storage room may be related to their presence in the sample. Many of the VOCs found in the sample were common solvents such as ethyl acetate and ethanol which are stored in the room. At least sixteen compounds were from chemicals stored in the room including hexane, acetone, carbon disulfide, toluene, cyclohexane, tetrachloroethylene, and phenol. Compounds such as ethylbenzene, the xylenes, nonane, and tridecane were among compounds stored in the laboratory but not in the storage room sampled. Ethanol is also an ingredient in cleaners and its presence can also be connected to any cleaning supplies used in the space.[186] While chemicals are stored in cabinets, with some being connected to ventilation, it is still possible that some of these compound escape and enter the laboratory air. While hexane and toluene are known artifacts of sorbent use, the responses present in this sample are higher than the normal artifact levels. Hexane and toluene are common solvents found in chemistry laboratories which were stored in this space. Therefore, the increased response of these VOCs can be linked to their presence in one of the storage cabinets in the room.

Several of these have been found in a previous study examining laboratory air including acetone, 3-methylpentane, 2-methylpentane, hexane, ethyl acetate, methylcyclopentane, heptane, benzene and toluene.[163] Many of these compounds are not a part of the target lists, and examples are ethyl acetate and cyclohexane which can cause irritation and narcosis.[187,188] In 2019, Sanchez found several VOCs such as acetone, 3-methylpentane, 2-methylpentane, hexane, ethyl acetate, methylcyclopentane, heptane, benzene, and toluene in the breath of the individuals working the laboratory.[163] While these many be specific to the location sampled, there may be other sources of VOCs that produce nontarget compounds which creates an issue for workplace monitoring if the analyst is only looking for specific compounds. Many of the compounds seen in this sample have also been seen in laboratory air samples collected by Wong and Webster.[189] Many of the compounds seen in Wong and Webster's work and those seen in this thesis are common chemicals in a research laboratory which explains their presence in the storage room air.

3.3.2.2 Harynuk Research Laboratory

The next indoor air sample was also collected in the Department of Chemistry in University of Alberta. Specifically, the Harynuk Group research laboratory air was sampled on a day with minimal experiments taking place to obtain the chromatogram in Figure 3.11. The sampling pumps were set in the middle region of the laboratory on an open bench and ran for one hour. The samples were collected on August 2, 2021, from 4:00 pm to 5:00 pm at a rate of 51.60 mL/min. During the 60 minute sampling time, a sample volume of 3.10 L was collected on the sorbent tube. Here like Section 3.3.2.1, there are chemicals present in the laboratory based on the nature of the research performed. There is chemical storage in the laboratory in cabinets in addition to the chemicals used in sample preparation which can provide a wide range of sources. Therefore, it is expected that there would be VOCs such as the alkanes, aromatics and common chemical solvents present from their use. Both Figure 3.11 and Table 3.5 give the some of the abundant VOCs from the sample collected from the bench in the laboratory. The intensity of the peaks present in the chromatogram is represented using the color bar on the left side of the figure.



1. Ethanol
2. Acetone
3. Butanenitrile
4. Isopropyl Alcohol
5. Methacrolein
6. Methyl Vinyl Ketone
7. 2-butanone
8. Hexane*
9. Ethyl Acetate
10. Tetrahydrofuran
11. Cyclopentane, methyl
12. Benzene*
13. 1,4-dioxane
14. Heptane
15. Toluene*
16. Octane
17. Hexanal
18. Tetrachloroethylene
19. Ethylbenzene
20. m-Xylene
21. o-Xylene
22. Cyclohexanone
23. Benzaldehyde
24. Octanal
25. Acetophenone
26. Tridecane
27. Decanal
28. Dodecanal

*- Known Artifacts

Figure 3.11: GC×GC-TOFMS Chromatogram of the Air Sample Collected in the Harynuk Laboratory Space

Table 3.5: Total Ion Chromatogram Data from TOFMS Results from Air Sample Collected in the Harynuk Laboratory Space

Compound Name	^1t_r (min)	^2t_r (s)	Area	Height	Width	Similarity	Reverse	RI	Lit. RI
Acetaldehyde	6.38	0.43	8.47E+05	32434.12	0.3005	893	935		
Ethanol	7.82	0.31	5.48E+07	1.68E+06	0.4336	918	919		
Acetone	8.95	0.92	6.10E+06	2.53E+05	0.2332	925	931		
Pentane	9.06	0.16	1.02E+06	66943.86	0.2005	893	928	500	500
Isopropyl Alcohol	9.08	0.37	3.59E+07	1.11E+06	0.3669	922	928	500.56	524
Isoprene	9.46	0.23	3.63E+05	21528.93	0.1337	831	924	510.10	520
Methylene chloride	10.48	0.32	3.30E+05	12741.99	0.1670	739	851	536.10	531
Pentane, 2-methyl-	11.65	0.19	6.51E+05	27066.13	0.1997	849	922	565.93	559
Methacrolein	11.88	0.71	9.07E+05	30442.01	0.2002	801	861	571.85	566
Pentane, 3-methyl-	12.29	0.19	1.58E+06	73661.26	0.2005	871	899	582.12	580
Methyl vinyl ketone	12.62	0.92	3.76E+06	1.04E+05	0.2668	896	952	590.45	606
n-Hexane	12.99	0.18	8.91E+06	5.23E+05	0.2005	939	945	600.00	600
2-Butanone	13.02	0.91	3.70E+06	1.15E+05	0.2335	899	932	600.58	602
Ethyl Acetate	13.78	0.61	5.63E+06	2.83E+05	0.2665	868	875	617.47	618

Cyclopentane, methyl-	14.49	0.20	1.99E+06	99112.62	0.1670	900	929	633.26	629
Tetrahydrofuran	14.56	0.50	2.05E+05	14400.08	0.0995	705	916	634.83	621
Benzene	16.14	0.35	9.40E+05	47509.89	0.1336	893	939	670.03	662
Hexane, 3-methyl-	16.43	0.18	2.69E+05	10975.95	0.2004	780	830	676.32	667
Pentane, 2,2,4-trimethyl-	17.02	0.21	3.68E+05	17029.28	0.1337	742	778	689.63	680
2-Pentanone	17.08	0.84	4.69E+05	14347.69	0.1666	717	835	690.92	687
Heptane	17.49	0.17	2.93E+05	14963.83	0.1672	775	829	700	700
1,4-Dioxane	18.20	0.55	2.95E+05	17781.96	0.1333	805	870	716.00	670
Cyclohexane, methyl-	18.91	0.20	4.01E+05	16127.66	0.2000	747	854	731.97	713
Heptane, 2-methyl-	20.43	0.16	5.32E+05	18912.68	0.1667	752	792	766.27	763
Toluene	20.93	0.31	2.00E+06	94726.67	0.2003	912	934	777.53	769
Octane	21.92	0.14	8.12E+05	42330.65	0.1336	826	897	800	800
Hexanal	22.09	0.65	3.16E+05	18490.93	0.1328	801	916	804.25	802
Tetrachloroethylene	22.89	0.24	7.27E+05	34088.02	0.1337	863	944	823.69	815.15
Octane, 2-methyl-	24.62	0.14	6.37E+05	23817.18	0.1999	765	814	865.70	864.9
Octane, 3-methyl-	24.95	0.14	3.26E+05	14200.18	0.1672	752	807	873.73	871.93
Ethylbenzene	25.02	0.27	1.02E+06	40907.32	0.1669	782	926	875.58	864.1
m-Xylene	25.32	0.27	4.05E+06	1.37E+05	0.2997	890	947	882.88	872.5
Nonane	26.03	0.12	1.64E+06	75490.56	0.1670	842	889	900	900

Styrene	26.26	0.31	1.89E+05	13001.76	0.1000	789	900	906.03	882
Heptanal	26.26	0.58	5.46E+05	16953.69	0.2336	787	844	906.09	901
o-Xylene	26.38	0.29	1.47E+06	48855.85	0.1997	887	925	909.35	908
Octane, 2,6-dimethyl-	27.39	0.13	5.35E+05	21841.98	0.1669	797	877	936.09	935.12
Nonane, 4-methyl-	28.40	0.11	5.03E+05	18206.39	0.1668	787	850	962.68	962
Decane	29.81	0.10	1.94E+06	86361.70	0.1337	882	918	1000	1000
Octanal	30.09	0.52	1.84E+06	71442.36	0.3330	892	941	1008.22	1005
Benzene, 1,3-dichloro-	31.18	0.31	1.50E+05	7841.51	0.1337	757	856	1039.44	1022
Benzene, 1,4-dichloro-	31.23	0.31	19528.01	3086.498	0.0667	569	601	1041.07	1021.24
p-Cymene	31.28	0.16	6.20E+05	18377.49	0.1334	631	674	1042.40	1026
Decane, 3-methyl-	32.33	0.11	3.44E+05	15404.46	0.1002	689	817	1072.52	1070
Benzene, 1,3-diethyl-	32.41	0.18	8.64E+05	25411.58	0.1336	757	833	1074.95	1056
Acetophenone	33.06	0.66	1.86E+06	74247.29	0.1995	880	914	1093.75	1078
Undecane	33.28	0.08	2.75E+06	1.08E+05	0.1671	863	892	1100	1100
Nonanal	33.64	0.47	3.53E+06	1.50E+05	0.2336	887	895	1111.18	1102
Decanal	36.94	0.43	1.19E+07	5.39E+05	0.2335	895	907	1214.67	1200
Naphthalene-D8	37.44	0.36	1.01E+07	4.19E+05	0.3000	862	900		
Tetradecane	42.41	0.05	2.85E+05	11410.88	0.1334	718	839	1400	1400

Dodecanal	42.93	0.36	7.75E+05	25209.17	0.3661	835	892	1417.02	1412

$^{1}t_r$ – First dimension retention time, $^{2}t_r$ – Second retention time, RI – Retention index, Lit. RI – Literature Retention Index

Looking at the retention indices of the compounds found here, many of the VOCs have values which are within a difference of ten or twenty compared to the known values. The mass spectral match factors for these analytes, except for p-cymene and 3-methyldecane, are above 700 which indicates a good match compared to the library search. The value for 1,4-dioxane's retention index shows a larger difference compared to known values which may be related to the lower response level for this compound leading to differences in the mass spectral identity. Looking at the response of naphthalene-D8, 1.01×10^7, it is significantly greater than the individual internal standard runs mentioned previously. This could be related to a potential difference in the volume spiked onto the sorbent tube, but this difference makes it difficult to determine if there was any sample loss. Like Figure 3.10, many of the compounds present in this sample are from common solvents used in chemistry research. These include methylene chloride, ethanol, ethyl acetate and acetone which are prevalent in the laboratory sampled in. The isopropyl alcohol can be related to the number of bottles placed in the room for cleaning as well as sanitization purposes.

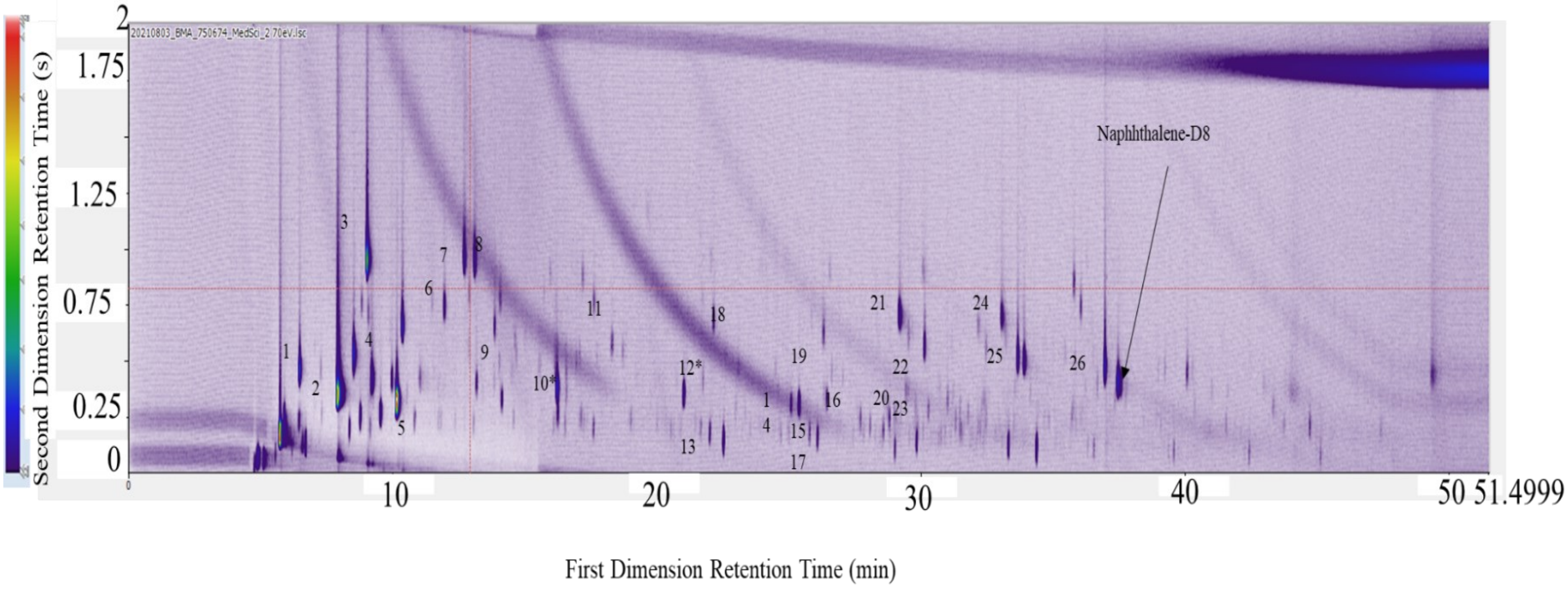
The target VOCs were calibrated using the thermal desorption calibration work performed in Chapter 2 for compounds in the calibration range. One of the target VOCs found in the air was tetrahydrofuran which was determined to be present at a concentration of 0.25 ppbv. Tetrachloroethylene was also detected in the sample and was measured at concentration of 0.07 ppbv in the air for this sample. The target aromatic hydrocarbons styrene, o-xylene, and p-cymene were measured at concentrations of 0.17 ppbv, 0.13 ppbv and 0.09 ppbv in the air respectively. These VOCs were at concentrations below the EPA range, similar to the other samples which further shows the benefit of this method due the ability to measure lower concentrations of VOCs. However, these results were impacted by the leak as well therefore the concentrations given here are likely not representative of the actual concentrations at the sampling site.

Previous work has linked significant levels of ethanol and isopropyl alcohol to standard cleaning supplies.[190] While these specific VOCs might be found normally in chemistry research laboratory, compounds such as this can be found anywhere due to their use in standard cleaning supplies. This a common exposure route of VOCs which presents a risk to the individual using the products at the time with others at a lower risk.[77] In relation to Figure 3.10, the two rooms are connected which explains the number of common compounds found in both samples. Previous studies looking at laboratory air quality found several VOCs common to those found in this sample, similar to the chemical storage room.[163,189] The VOCs found in this sample consist of primarily of those not on the target lists that the agencies such as the US EPA typically look for when monitoring. The health effects of a couple of these have been touched on with previous samples such as ethyl acetate and nonane.

Additional indoor air quality studies found many compounds such as the aldehydes, alkanes and aromatics in a large hospital complex.[111] While the location is different from this sample, there are a large portion of common compounds which could be a result of common sources such as fragrance products or the presence of any petrochemical products.[111] The laboratory sampled does have petrochemical products in storage and fragrance products could be present on individuals present as well as in scented products in the room. Several compounds present such as dichloromethane, tetrahydrofuran, 2-butanone, 2-methylpentane and 3-methylpentane can be a result of a variety of sources such as paints, waxes, adhesives or cleaning products.[191] In this particular laboratory, dichloromethane or methylene chloride is commonly used a solvent which can also explain its presence in the air. A couple of the compounds seen here, such as acetaldehyde and pentane fall into a category called verry volatile compounds or VVOCs which is not well regulated or defined created further problems for monitoring.[191] Pentane presents risk of irritation and drowsiness when exposed while acetaldehyde can lead to coughing and central nervous system problems.[192,193] Furthermore, acetaldehyde has the potential to cause cancer or cause birth defects when individuals are exposed.[192,194] Acetaldehyde was identified in nearly all samples analyzed which presents a risk as this can have serious health effects but it may not be included in standard reports as it is not a target compound. The fact that these compounds are not a part of standard monitoring procedures could present an issue if these compounds are missed in reporting.

3.3.2.3 University of Alberta Medical Sciences Building

The University of Alberta's Medical Science Building was sampled in addition to the different locations in the Department of Chemistry at the University of Alberta in Edmonton AB, CA. In particular, the sampling pumps were set up in a hallway outside an anatomy laboratory on the sixth floor of the building and the results of which is shown Figure 3.12. The sample was collected on August 3, 2021, from 1:06 pm to 2:06 pm at a rate of 50.33 mL/min. During the 60-minute sampling time, a sample volume of 3.02 L was collected on the sorbent tube. The chromatogram in Figure 3.12 and results in Table 3.6 details the results from the air sample collected in the hallway. The sampled hallway had little activity due to sampling taking place in the summer when there are less students present. Here since this was a hallway not a laboratory, it was not expected that there would be many VOCs present in the air sample.



1. Acetaldehyde
2. Ethanol
3. Acetone
4. Isopropyl Alcohol
5. Methane, Ido
6. Methacrolein
7. Methyl Vinyl Ketone
8. 2-butanone
9. Ethyl Acetate
10. Benzene*
11. Pentanal
12. Toluene*
13. Octane
14. Ethylbenzene
15. m-Xylene
16. o-Xylene
17. Nonane
18. Hexanal
19. Heptanal
20. Camphene
21. Benzaldehyde
22. Octanal
23. Benzene, 1,2,4-trimethyl
24. Acetophenone
25. Nonanal
26. Decanal

*- Known Artifacts Compounds

Figure 3.12: GC×GC-TOFMS Chromatogram of a Sample Collected from Hallway in Medical Sciences Building at University of Alberta

Table 3.6: Total Ion Chromatogram Data from TOFMS Results from the Sixth Hallway of the University of Alberta's Medical Sciences Building

Compound Name	^1t_r (min)	^2t_r (s)	Area	Height	Width	Similarity	Reverse	RI	Lit. RI
Acetaldehyde	6.47	0.46	4.23E+06	2.22E+05	0.3003	966	967		
Ethanol	7.91	0.35	3.13E+07	1.01E+06	0.4335	943	943		
Acetone	9.02	0.94	1.55E+07	5.75E+05	0.2666	941	945		
Isopropyl Alcohol	9.20	0.41	2.07E+06	54619.75	0.3669	881	958	501.74	524
Methane, iodo-	10.15	0.32	3.02E+07	1.19E+06	0.2669	934	935	525.98	530
Methacrolein	11.95	0.74	6.67E+05	21767.73	0.2000	817	886	571.85	566
Methyl vinyl ketone	12.69	0.95	1.79E+06	39637.36	0.2331	871	942	590.61	606
2-Butanone	13.09	0.94	1.69E+06	11540.65	0.1670	798	891	600.70	602
Benzene	16.22	0.38	3.40E+06	1.28E+05	0.2333	936	948	669.81	662
Toluene	21.01	0.35	9.27E+05	38252.59	0.2002	848	865	777.95	769
Octane	21.99	0.18	3.06E+05	13913.82	0.1673	794	880	800	800
Hexanal	22.12	0.68	1.26E+05	8525.911	0.1000	714	865	803.45	802
Ethylbenzene	25.08	0.30	3.59E+05	12576.25	0.1334	566	861	876.08	864.1
m-Xylene	25.37	0.31	7.60E+05	27594.2	0.1667	746	914	883.40	872.5
Nonane	26.07	0.16	4.29E+05	17702.57	0.1336	771	890	900	900

Styrene	26.31	0.33	50269.98	2670.633	0.1334	559	849	907.06	882
o-Xylene	26.44	0.33	1.24E+05	9174.263	0.1000	754	906	910.44	908
Camphene	28.79	0.24	2.41E+05	8688.741	0.1664	769	848	973.00	951
Benzaldehyde	29.18	0.70	1.53E+06	39178.28	0.3332	875	908	983.29	972
Benzene, 1,2,4-trimethyl-	29.22	0.24	63883.2	2338.135	0.2011	519	638	984.34	972
Decane	29.82	0.14	3.69E+05	16360.78	0.1338	796	860	1000	1000
Octanal	30.12	0.56	6.50E+05	19331.78	0.2335	833	904	1008.93	1005
Acetophenone	33.05	0.70	9.10E+05	19859.58	0.2331	803	863	1093.79	1078
Undecane	33.29	0.12	5.08E+05	24720.45	0.1336	800	857	1100	1100
Nonanal	33.65	0.51	1.43E+06	48763.78	0.2002	840	859	1112.07	1102
Decanal	36.95	0.47	2.97E+06	90636.74	0.2002	866	887	1214.96	1200
Naphthalene-D8	37.45	0.40	4.03E+06	1.23E+05	0.3999	831	875		

$^{1}t_r$ – First dimension retention time, $^{2}t_r$ – Second retention time, RI – Retention index, Lit. RI – Literature Retention Index

Looking at the match factors for this sample, most of the VOCs show high match factors but styrene and 1,2,3-trimethylbenzene show lower values. However, these compounds have lower areas, and this indicates lower amounts are present which can affect the match factor. The retention index values for the compounds in this sample are within a difference of ten or twenty when compared to known values for these VOCs. As a result of this, the identities determined by the mass spectral library search are reasonably accurate for the compounds present in this sample. Examination of the response of naphthalene-D8 for potential loss during the sampling process it is tricky as this sample has a response higher than initial internal standard runs. As the response is not less than the initial runs it would indicate that there is no loss however the fact the response is greater makes it difficult to concretely determine. The sampling site in this case was not location with direct contact large quantities of chemicals unlike the previous two indoor samples. The lack of larger quantities of chemicals present at the sampling site can be connected to decreased number of compounds found in the sample. This can indicate improved air quality over sites with increased number of VOCs present in the air. Furthermore, the sampling site was fairly empty during the sampling time meaning there few individuals walking by and the little activity taking place.

Like the other samples shown here, the target VOCs could be quantified using the thermal desorption calibration work performed in the previous chapter. One of the target VOCs seen in this sample was ethylbenzene which was determined to be at a concentration of 0.12 ppbv in the air. Further examination showed that styrene and o-xylene were both present in the air at concentrations of 0.12 ppbv. 1,2,4-trimethlybenzene was measured at a concentration of 0.08 ppbv in the air in the Medical Science hallway in the University of Alberta. Each of these VOCs were at concentrations below the EPA range which enable VOCs to be measured at lower levels. As with the other field samples shown in this chapter, this sample was affected by the leak in the system as analytes could have been lost during the analysis. As a result, the concentrations given here may not be completely representative of the VOC concentrations at the sampling location.

Looking at the aldehydes present in the sample, this can be related fragrances products used in the general area or on the nearby individuals.[111] Another compound potentially related fragrances products or deodorizers is camphene, a type of terpene, which is found in this sample as well.[186,190] These can be connected to the individuals that were present in the hallway during the sample time. Aldehydes have also been connected to wood products, such as pressed wood, and the samplers were placed on a table which may have contained pressed wood on the surface.[195] The sorbent tubes were placed directly on the surface of the table which brought them close to a potential source of VOCs. Solvents such as ethanol and isopropyl alcohol are ingredients in cleaning products so the presence of these VOCs many be related to cleaning of hallway or nearby rooms.[190]

Since the sampling site did not have as many chemicals present, unlike the containers present in the other locations, these solvents are likely from maintenance staff cleaning the area before the sampling taking place. Alkanes and aromatic compounds are typically associated with vehicle exhaust or petrochemicals but a possible source of these VOCs could have been a partially open window in the hallway letting VOCs from the road below in.[111,196] Petrochemicals have been seen in a hospital complex in a Swedish study indicating that these compounds can be found in locations other than those which have fuel sources present.[111] Though the levels of benzene and toluene are impacted by the fact that these are known artifacts from sorbent use. Building materials may contribute to the presence of VOCs in the air and the alkanes and 1,2,4-trimethylbenzene have been connected to the walls or floors of buildings.[186] Methyl vinyl ketone has also been connected to building materials off gassing as well as possibly from bleach use.[186] VOCs from building materials may always be present due to the products which make up the space and this should be considered when looking at the compounds present.

3.3.2.4 Indoor Air Sampling Summary

For testing the method for indoor air quality sampling, twelve indoor locations at the University of Alberta were sampled, three of which were shown previously. These locations ranged from offices to chemical storerooms. Most of the locations were in the University of Alberta's Department of Chemistry and the only location outside of this department being a hallway in the University of Alberta's Medical Sciences Building. The Department of Chemistry locations generally had more VOCs present due to the nature of the work in these locations compared to the Medical Sciences Building hallway. A summary of the most abundant compounds found in the locations sampled is shown in the graph in Figure 3.13 which displays the number of different compound classes found in each sample.

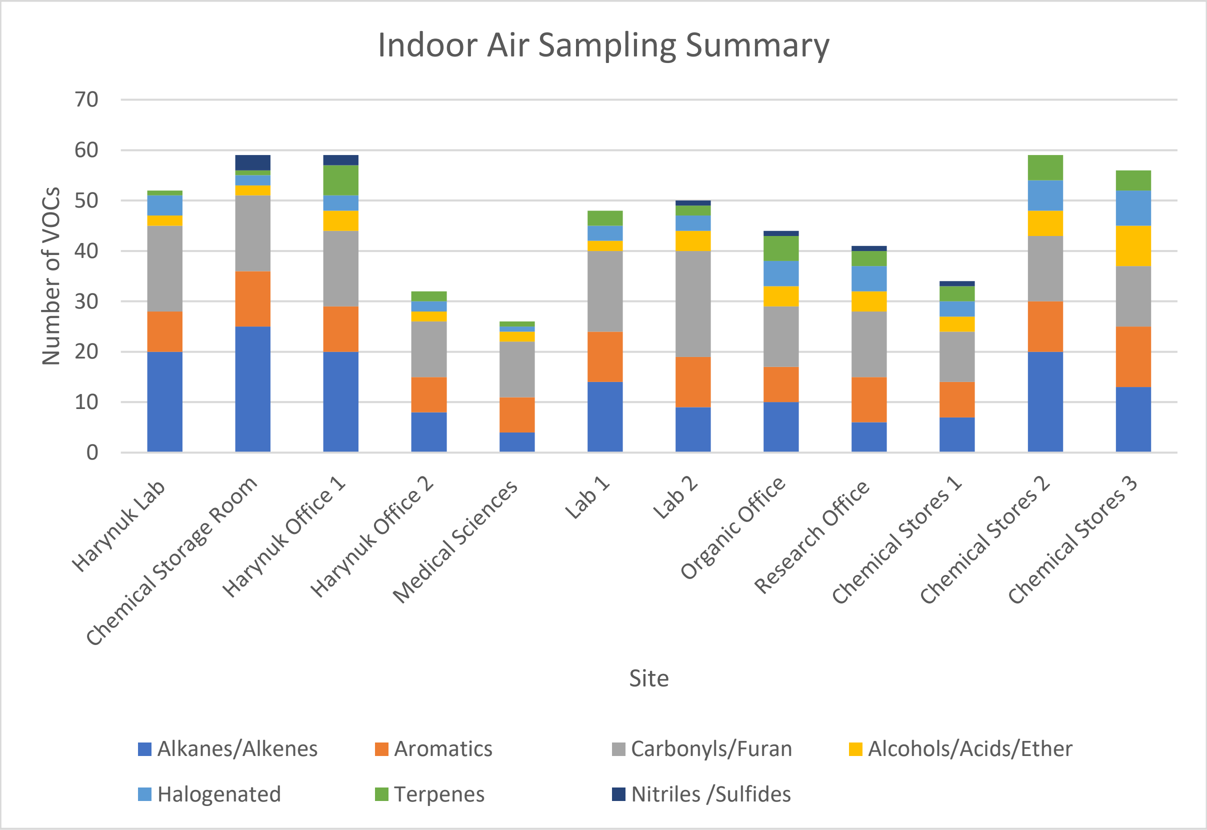
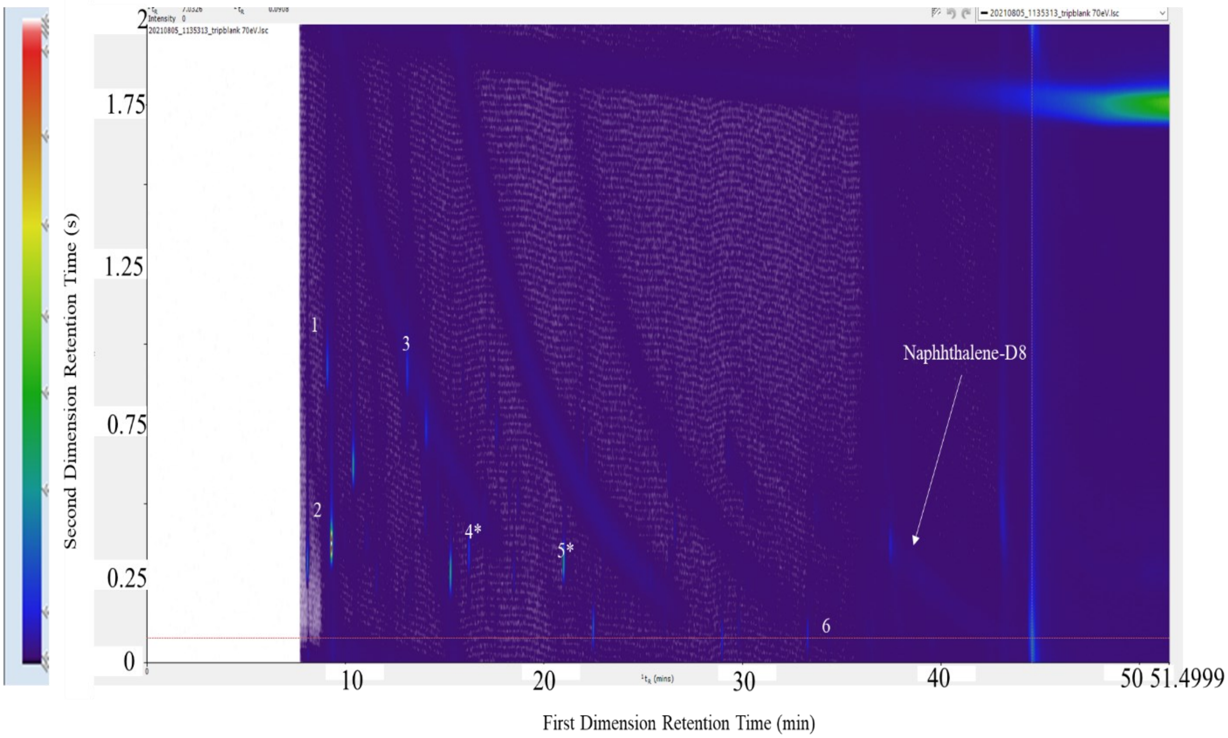


Figure 3.13: Summary of the Most Abundant VOCs Present in the Indoor Air Samples

The location with the lowest number of VOCs present was the Medical Sciences building with one of the Harynuk Offices having the second fewest number of compounds. This can be related to the fact that in both locations, unlike most of the other sites, chemicals were not present in significant quantities. Except for the offices sampled, many of the sites were chemistry research laboratories or chemistry storerooms which can contribute to airborne VOCs. The number of VOCs in Harynuk Office 1 was like several of the sites which had chemicals present such as storerooms. A significant number of these VOCs were carbonyl compounds which have been linked to dry erase markers.[197] The samplers were set up next a white board which had several markers present as well as writing on the board. The presence of the xylenes in several locations can be connected to markers as well.[197] The most abundant compounds present in these samples were either the alkane/alkenes or carbonyl/furan compounds. Locations with the most abundant compounds being alkanes/alkenes were sites which had chemicals present or nearby in storage units. The Chemistry Stores sites had significant levels of chemical solvents and at two of the Chemistry Stores locations the VOCs were at detectable by odors in the rooms. Two of the locations are used for preparation chemicals or solutions for undergraduate organic chemistry laboratories which presents a source for VOCs in the space. Halogenated compounds can also be contributed to solvents used in the research laboratories or kept in the storage rooms. An example of a common solvent is dichloromethane which was frequently found in these sampling sites.

For other locations, the most abundant compounds were aldehydes which have been connected to fragrance products.[111] Several sites had terpenes present which have also can be connected to fragrance products or deodorizers being used in the area.[186] These VOCs may be present on individuals working in the spaces due to products they use on a daily basis. Aldehydes and terpenes have also been seen in in restaurants as a result of food being repared.[170,194] Therefore, it is possible that if food was prepared in some way or present then these compounds could be introduced as a result. All the locations had similar amounts of aromatic VOCs present in the air regardless of the type of sampling site. Bari et al. saw various aromatic compounds from flooring or wall materials which could an additional source of these compounds in this case as well.[186] While in the chemical storage areas, these will also come from the presence of the chemical bottles in the room as well. The organic chemistry office was located near a building entrance which was undergoing construction at the time. This introduces an additional source of aromatic VOCs from the exhaust of construction vehicles or activities.[77] Compound classes which were not seen in the outdoor samples were the nitrile compounds as well as sulfur containing VOCs. These were primarily found in the research laboratories or chemistry storage rooms, even the organic chemistry office has a room for some chemical storage. There was overlap between the VOCs found in the indoor locations and the outdoor sites but the difference between the two is the type of sources of VOCs.



1. Acetone
2. Isopropyl Alcohol
3. 2-butanone
4. Benzene*
5. Toluene*
6. Undecane

*-Known Artifact Compounds

Figure 3.14: GC×GC-TOFMS Chromatogram of a Capped Universal Sorbent Tube Used as a Trip Blank

Figure 3.14 shows an example of a trip blank used when collecting indoor air quality samples, like the outdoor air samples. This sorbent tube remained sealed in the travel container during the entire sample trip and any compounds found would be as result of artifacts from the sorbent tube or from travel. For most of the trip blanks, the sorbent tubes showed primarily artifact compounds; hexane, benzene and toluene with other compounds being present at low levels. Specifically looking at acetone and isopropyl alcohol, these are at much lower levels compared to sampled sorbent tubes. One of the trip blanks used to examine any contamination from transport for samples collected in the Chemistry Stores in the Department of Chemistry showed a greater number of compounds compared to other blanks. Several VOCs were present in the sorbent but the response levels for these compounds are generally lower compared to sampled sorbent tubes. The presence of these compounds can be a result of slight difference in the sealing of the sorbent tube for transport. In this case, the responses of several of the VOCs in the samples collected in the Chemistry Stores can be attributed to the transport of the sorbent tubes. However, the responses from the sampled sorbent tubes at these sites were significantly greater than the responses present in the blanks. Therefore, many compounds seen are from the VOCs present at the site not from transport.

3.4 Conclusions

Air quality monitoring is needed in both indoor workplaces and outdoor ambient air because of a range of sources emitting VOCs in the air. This chapter explored possible applications of the previously developed hybrid method to see the nontarget capabilities it provides over standard one-dimensional gas chromatography methods. With the nontarget portion of the method, compounds not on standard target lists can be seen more easily due to the separation power of comprehensive two-dimensional chromatography. Seven different outdoor locations were used to examine air quality at various sites. These included constructions sites which could emit VOCs from exhaust, roadsides presenting vehicles as a source, an apartment balcony near a main road and a local park upwind from an industrial area. These locations were chosen due to the potential to have VOCs present due to the emission sources at each site. Here many of the compounds were not a part of target lists which would normally go unreported.

Of the more abundant VOCs present in the samples, the alkanes were the most prevalent in many of the samples analyzed. The next most abundant VOC class in the outdoor sampling sites were the carbonyl compounds, specifically the aldehydes. This overlap can be a result of common emission sources present at the different sites. The position of the sampling devices had a moderate impact on the number of VOCs present on the sorbent tube as sites closest to emission sources such as roadways and construction sites had more VOCs. Locations where the sampling devices were placed further away from the sources, typically due to lack of access, showed lower numbers of VOCs present. This could be attributed to wind conditions sweeping the VOCs in a different direction away from the sampling location. Individuals close to the source of the VOCs are at greater risk for health effects from these compounds as there are higher levels when at the source. One of the sampling locations, an apartment balcony, had a significant number of compounds despite being further from roadways. This can be related to wind conditions moving emissions from the nearby hospital or other businesses as the balcony faced the University of Alberta Hospital. In general, the VOCs found in each sample matched the various emission sources at the sites such as vehicles or biogenic compounds.

To examine workplace air quality, indoor locations were sampled around the University of Alberta, specifically the Department of Chemistry and the Medical Sciences Building. These included chemistry research laboratories, offices, chemical storerooms, and public hallways which each presented different possibilities for VOCs. Many of the locations had chemicals present in the room or in chemical storage cabinets which can emit VOCs in the air. In a couple of the locations, the VOCs could be detected due to an odor present. These rooms were used for preparing for undergraduate organic chemistry laboratories which explains the presence of many of the VOCs in these spaces. In these room, there is a higher exposure risk for these solvents presenting a health risk for these individuals. Several of the laboratories sampled are well ventilated which can aid in reducing the exposure to VOCs compared to other locations.

Many of the VOCs found in the indoor spaces were chemical solvents which in many of the cases can be attributed to solvent use in the laboratories or in storage. However, VOCs can come from other products which presents risks in workplaces other than laboratories because of common activities such as cleaning or even food preparation.[186] The location with the lowest number of the significant VOCs was in the Medical Sciences Building and this can be related to the lack of chemicals in the vicinity unlike in the research laboratory locations. Common VOCs between the outdoor and indoor locations are the alkanes, aromatics, aldehydes, and terpenes; however, the major difference is the source of the VOCs. A noticeable difference between the two was the increased number of carbonyl compounds present, primarily due to the increased number of aldehydes. These can be linked to fragrance products present both in the rooms and on individuals who work in the space.[111] The indoor locations sampled here were primarily laboratories or support rooms which present different risks then other locations. Both indoor and outdoor locations can have a range of VOCs present, some are more harmful than others, thus the nontargeted aspect of the developed method is vital to environmental monitoring. It is important to restate the impact of the leak on these results as the responses could appear to be lower than the amounts actually present at the sampling site. This resulted in the underreporting of the

VOCs present in at the sampling site which may lead to compounds being falsely reported at safe levels. Because of the leak, the quantitation results are not completely representative of the concentrations at the sampling site due to the loss of analytes during analysis. A significant number of compounds seen in the samples were nontarget compounds which meets the hypothesis of the chapter. The ability to see VOCs such as acetaldehyde and the alkanes can allow for improved monitoring as well as improved regulation of emissions.

Chapter 4 Conclusions and Future Work

4.1 Conclusions

The complexity of air requires new methods to fully understand the number of VOCs present in samples collected for both outdoor air quality and occupational air studies. There are many VOCs that governmental agencies currently monitor for in the atmosphere, however, these are just the tip of the iceberg. Unknown compounds, VOCs that are not currently monitored, can present a risk for individuals exposed to if they go unreported. To fill this gap in the environmental air monitoring field, a hybrid targeted-nontargeted method has been developed using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry. This instrumentation has increased separation power due to the additional dimension added through the second analytical column which enables nontargeted analysis. Here compounds that would coelute in traditional methods can be separated which leads to the better detection of unknown compounds. The time-of-flight mass spectrometer allows for identification of the nontarget VOCs which makes the instrumentation a powerful tool for environmental air monitoring.

The developed hybrid targeted-nontargeted method included thermal desorption which simplifies the sample preparation process and enhances the analyte signal.[94] Here sorbent tubes were used for active air sampling then thermally desorbed to introduce the VOCs to the GC×GC-TOFMS system for analysis. Alternative methods of sample preparation can introduce health risks or increase the total analysis time due to lack of automation which can be significant disadvantages for commercial laboratories.[94] The simplified sample preparation process allows for the sorbent tube to be immediately placed into the instrument for analysis without lengthy preparation or solvent use. The combination of both types of instruments creates an opportunity to both see the full range of VOCs present in the sample and fully automate the analysis process.

The optimized method addressed the needs of both targeted and nontargeted work through the careful selection of column sets and method parameters. Due to the high volatility of the analytes, columns with increased film thickness, 1.0 µm and 0.50 µm, were used to facilitate better resolution between compounds. Proper sampling of the first-dimension column effluent was found at a modulation period of 2.0 s as increased modulation periods resulted in loss of resolution due to under sampling. This lower modulation period allows for better detection of analytes as the resolution from the first dimension separation will be preserved which prevents coelutions and analytes being missed. Desorption conditions were carefully considered to ensure that the sample was completely desorbed from the sorbent tube for accurate quantification of the VOCs of interest and detection of nontarget VOCs. These conditions were found to be desorbing the sorbent tube for ten minutes at 250 ℃ with helium carrier gas flowing through at rate of 50 mL/min for the sorbent tube desorption. Conditions for the complete desorption of the focusing trap were determined to be starting the trap at -25 ℃ then rapidly heating to 300 ℃ for three minutes with a 20:1 split. The split during focusing trap desorption was used to facilitate complete desorption by increasing the total flow rate through the focusing trap.

For validation and quantification purposes, calibration curves were generated for a series of target VOCs using the responses from the 70 eV TOFMS data from a series of seven standards. The two methods of injecting the standards were 1 μL liquid injections using an autosampler and loading 1 μL onto the sorbent tubes then thermally desorbing them. Using the calibration curves' slopes, the limits of detections and limits of quantification for the target compounds were calculated. Examination of the limits of detection values for the target compounds showed that in many cases the thermal desorption method gave lower values compared to standard liquid injections. The other compounds showed comparable limits of detection between the two methods. For the thermal desorption method, the limit of detection values ranged from 0.0009 ng on column to 0.02 ng on column using a 20:1 split ratio. The limits of quantification showed a similar trend to the limit of detection values between the two methods. Here, for the thermal desorption method, the limit of quantification values ranged between 0.003 ng on column to 0.07 ng on column with a 20:1 split ratio. The calibration work was completed after the leak was discovered; however, some error may have occurred in setting the split flow in the thermal desorption unit. The method developed here was able to provide enhanced sensitivity because of both techniques used, comprehensive two-dimensional gas chromatography and thermal desorption.

An additional advantage of this hybrid method is the ability to perform nontargeted analysis and the TOFMS detector allows for tentative identification of these VOCs. However, it may be desirable to determine the relative amount of the VOCs found through nontargeted analysis. This instrument had a flame ionization detector which can be used to quantify these nontarget VOCs using response factors. Responses in the flame ionization detectors are comparable between different compounds which enables nontarget quantification more easily than it would be with time-of-flight mass spectrometers. Furthermore, it was seen that care is needed when storing sampled sorbent tubes to ensure sample loss does not occur. While no clear benefit was seen to using refrigerated conditions, it is possible that moving to lower temperatures, 0℃ or lower, can help increase the amount of time sorbent tubes can be stored. It was seen that to ensure that sampled sorbent tubes retain their integrity for accurate analysis that these multisorbent tubes should not be stored for longer than two weeks. If there is more than one sorbent is packed inside the tube there is a risk of analytes moving to stronger sorbents and being permanently adsorbed.[93] There is a benefit to using multisorbent tubes as they enable larger ranges of VOCs to be sampled which can be helpful when the exact composition of the samples are unknown. If the analyst decides this is needed for the analysis, care is needed when using these sorbent tubes in storing them to maintain sample integrity. The storage time seen here was shorter than seen in other works. This can be connected to several sources including the leak in the system, human error, and analytes either migrating to stronger sorbents or not reaching the proper sorbent.

Field samples studied showed a wide variety of VOCs present in both indoor and outdoor locations with a significant number of these VOCs being nontarget compounds. Compounds such as alkanes, aldehydes and terpenes were common at the sampling sites, but these may be missed in standard methods. Outdoor locations had an abundance of alkanes and aromatics present while indoor locations showed significant amounts of alkanes as well as carbonyl compounds. Outdoor sampling sites are exposed to biogenic compounds from vegetation as well as fuel exhaust from vehicles. Many of the indoor sampling sites were exposed to solvents and other common chemicals. In a couple of the rooms sampled there was an odor present which was likely a result of the chemicals in the space. In many cases, the number of VOCs found in the samples were greater when the sampling pumps were set up closer to emissions sources. These samples showed that individuals such as construction workers, laboratory workers, and transit personnel have increased exposure to air pollution such as VOCs. A source present in the indoor sampling sites was cleaning products and while no cleaning took place during sampling, the VOCs may still be present well after cleaning taking place.

An additional source comes from materials such as wood, walls, paints, vegetation, and flooring materials which can off gas VOCs in the air meaning that these compounds may always be present in the air. These field samples were able to show the benefit of using a hybrid targeted-nontargeted method for environmental air monitoring as there were many compounds that were not a part of monitoring lists. In some cases, there is the chance to add new compounds to lists which can aide methods using one-dimensional gas chromatography. While the target lists are useful for monitoring the compounds known to impact human health or the environment, a deeper look into the sample can reveal hidden pollutants. The developed hybrid targeted-nontargeted method enables a deeper look into the sample though the ability to see the full sample profile.

The presence of the leak during most of the experimental work performed here impacted several aspects of the results shown in this thesis. Liquid injection work was not affected by the leak as it was only present in the thermal desorption system therefore only the thermal desorption experiments were impacted. The calibration work was repeated after the leak was discovered and because of this the LOD values as well as the LOQ values provided here were unaffected by the leak. It is possible that the desorption optimization work could have been impacted by the leak as low-level analytes present could have been lost. The experiments affected the most by the leak were the storage study and the field samples collected. In the former, the leak led to variations between replicates which would indicate instabilities in response due to storage while in the latter the leak caused underrepresentation in quantification. The underrepresentation in quantification was likely seen in both targeted and nontargeted quantification. The method developed in this thesis enables the analyst to take deeper look into ambient air samples to fill the gap in current environmental air monitoring methods. Overall, despite the presence of the leak, the goal of the thesis was met with the development of the hybrid targeted-nontargeted method using TD-GC×GC-TOFMS for environmental air analysis. A significant number of compounds present in the field samples were nontarget VOCs which shows that this method would be beneficial for environmental air monitoring which shows that the hypothesis from Chapter 1 was met.

4.2 Potential Future Work

4.2.1 Passive Sampling

The work in this thesis was performed using active sampling with sorbent tubes, then performing analysis using the developed hybrid targeted-nontargeted method. However, there are other means of sampling which can be employed to determine the VOCs present in the air. While active sampling is important for determining the VOCs present during brief exposure periods, passive sampling can provide insight into the VOCs present over a long period of time.[90,99,198] Here the VOCs present in the air are sampled on the sampler using the process of diffusion rather than an air pump.[90,199] Long term exposure studies allow for changes in VOCs levels to be seen over a period of days, weeks or even months.[90,116] It is important to note that diffusion takes time to complete the sampling process which is why this method is not used for short term sampling.[199,200]

Passive samplers allow for personal exposure monitoring over a period of weeks or months without additional equipment. These passive sampling devices do not require power supplies or sampling pumps while also being small in size.[90,198,200] The simple sampler design along with the ease of use presents significant advantages for environmental air monitoring as minimal training is needed for their use. Passive sampling devices range from single sorbent tubes, wristbands, the Waterloo Membrane Samplers and Radiello samplers which gives flexibility to analyst developing sampling campaigns.[90,148,198,201] Using a hybrid targeted-nontargeted method in long term exposure studies can reveal important information just as it can with short term campaigns. Two examples of passive samplers are shown in Figure 4.1, the Waterloo Membrane Sampler is shown on the left and the single sorbent tube. These samplers are taken to the sampling location and exposed to the air for predetermined amount of time to preform long term exposure studies.

Figure 4.1: Examples of Passive Samplers: The Waterloo Membrane Sampler (left) and a Single Sorbent Tube (Right)

To apply this analytical method to long term exposure studies, the passive sampling method must be determine using controlled experiments. This is possible with an experimental set up which can create gaseous mixtures of VOCs and then have the samplers exposed to this mixture. The groundwork for developing this experimental set up has been laid through the development of a permeation chamber for creating controlled gas mixtures of VOCs. Permeation devices have also been designed to create the mixtures of VOCs in the permeation chamber. Figure 4.2 shows the design for the lab-made permeation chamber for generating gas mixtures in a controlled manner. Here clean air is flowed through tubing to enter the chamber at a user set rate by the mass flow controller. The air is produced by a laboratory generator which provides clean air to the chamber. The chamber itself is seated on a hotplate which can be set to a temperature to enable evaporation of the VOCs while the chamber is undergoing air flow. Insulation wrapped around the chamber to ensure the entire system is heated evenly to allow for consistent permeation rates. The entire set up is connected to building air ducts to send excess VOCs to vent. Permeation devices can be placed in the glass chamber over a period of at least twenty-four hours and then the permeation rate of the chemical in the device is used to determine the mass in the air.

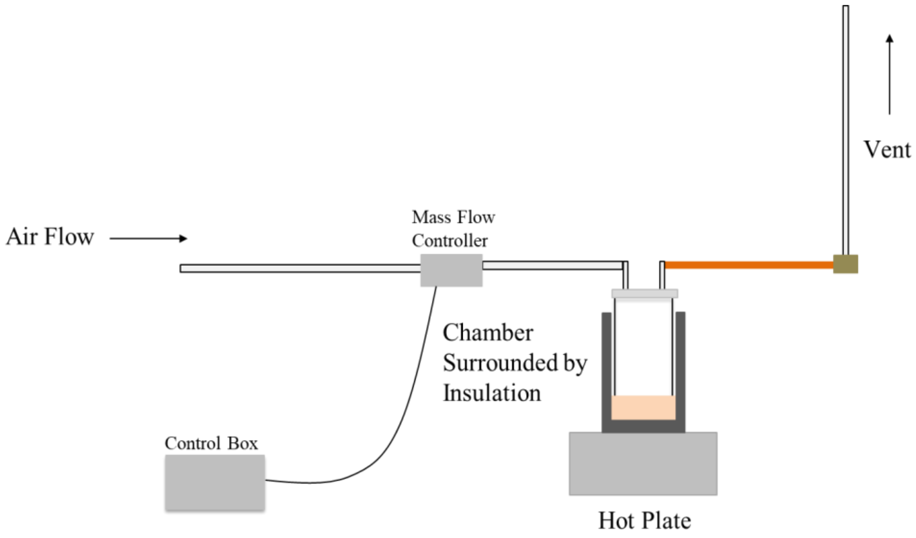


Figure 4.2: Schematic of a Permeation Chamber Set Up for the Generation of Controlled Gas Mixtures of VOCs

The permeation rate of the compounds can be determined gravimetrically by recording the mass of the permeation devices prior to being placed in the chamber and then after. The mass difference between the two measurements is the amount that permeated through the device and dividing the mass lost by the time in the chamber which results in the permeation rate. This value can then be used to determine the amount present in the chamber for the compounds in the gas mixture. Key here is that there is some solution remaining in the device after it is removed from the chamber as the permeation rate calculation will be more accurate. The permeation rate of the chemicals or mixtures in the devices can be altered, if different concentrations are needed, by changing the air flow or the temperature of the hot plate. The devices used here can be filled with any volatile chemical or mixture which gives a significant advantage to their use. This gives flexibility in what VOCs can be placed in the chamber and it also presents the opportunity to use mixtures such as gasoline or diesel. This flexibility allows for the ability to introduce passive samplers to different environments and test the samplers with different mixtures of VOCs. Work has been done on the optimal materials for these permeation devices to allow for ideal permeation rates of chemicals. The optimal materials were found to be Teflon tubes capped with steel screws as they were found to slow the permeation of the VOCs. The thick wall of the

Teflon tubing allows for the slow permeation rates and if the tube is properly sealed than there will be some solution left in the device which enables permeation rates to be calculated.

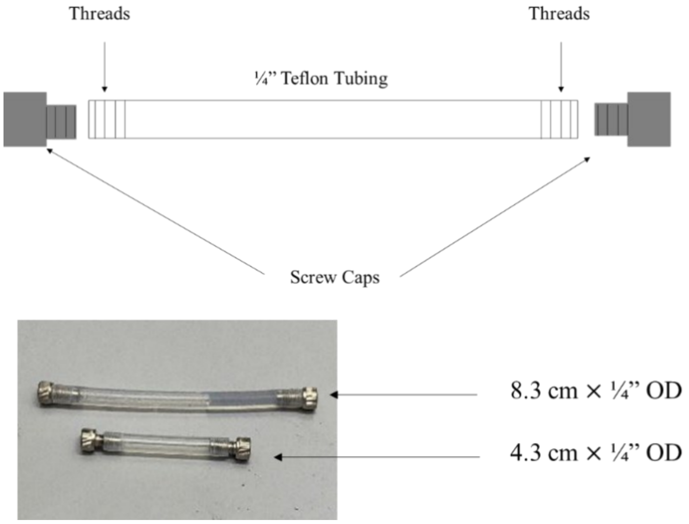


Figure 4.3: Permeation Tube Design Schematic (Top) and Image of the Teflon Permeation Tubes (Bottom)

Figure 4.3 shows the design of the Teflon permeation devices for creating controlled mixtures of VOCs in the chamber. The screw caps can be tightened using a Robertson screwdriver which creates a seal preventing loss of VOCs through the ends of the device. As shown in the bottom of Figure 4.3, two different lengths were developed to account for different volatilities. The larger device provides a greater surface area for semi-volatile compounds to be exposed to which leads to increased permeation rates. In contrast, the smaller device is used with more volatile compounds as the lower surface area will give lower permeation rates compared to the larger device. This can be beneficial for high volatility VOCs which would permeate at high rates in the larger tubes where it is possible for the chemical to permeate a rate fast enough that there is none left in the device. This results in inconclusive permeation rates which are necessary to determine the mass present in the chamber when the sampler was exposed. These devices and the constructed permeation chamber both enable future work in developing passive air sampling methods. These methods can then be applied to field sampling to study the VOCs present over days, weeks, or months. Coupling the thermal desorption-comprehensive two-dimensional gas chromatography hybrid method to passive air sampling can reveal hidden compounds present in the environment over long periods of time. The ability to determine all VOCs present in the sample during both long-term and short-term exposure studies using a hybrid targeted-nontargeted method is invaluable as missed VOCs can lead to potential health risks.

References

(1) Montero-Montoya, R.; López-Vargas, R.; Arellano-Aguilar, O. Volatile Organic Compounds in Air: Sources, Distribution, Exposure and Associated Illnesses in Children. *Ann. Glob. Heal.* **2018**, *84* (2), 225–238. https://doi.org/10.29024/aogh.910.

(2) Michulec, M.; Wardencki, W.; Partyka, M.; Namieśnik, J. Analytical Techniques Used in Monitoring of Atmospheric Air Pollutants. *Crit. Rev. Anal. Chem.* **2005**, *35* (2), 117–133. https://doi.org/10.1080/10408340500207482.

(3) Kampa, M.; Castanas, E. Human Health Effects of Air Pollution. *Environ. Pollut.* **2008**, *151*, 362–367. https://doi.org/10.1016/j.envpol.2007.06.012.

(4) Curtis, L.; Rea, W.; Smith-Willis, P.; Fenyves, E.; Pan, Y. Adverse Health Effects of Outdoor Air Pollutants. *Environ. Int.* **2006**, *32* (6), 815–830. https://doi.org/10.1016/j.envint.2006.03.012.

(5) Armenta, S.; de la Guardia, M. *Pollutants and Air Pollution*; Elsevier Ltd, 2016; Vol. 73. https://doi.org/10.1016/bs.coac.2016.03.002.

(6) El Morabet, R. *Effects of Outdoor Air Pollution on Human Health*, Second Edi.; Elsevier, 2019; Vol. 2. https://doi.org/10.1016/B978-0-12-409548-9.11509-X.

(7) Forbes, P. Atmospheric Chemistry Analysis: A Review. *Anal. Chem.* **2020**, *92*, 455–472. https://doi.org/10.1021/acs.analchem.9b04623.

(8) Hyötyläinen, T.; Kallio, M. Air and Aerosols. In *Comprehensive Analytical Chemistry*; 2009; Vol. 55, pp 167–187. https://doi.org/10.1016/S0166-526X(09)05508-1.

(9) Muscalu, A. M.; Górecki, T. Comprehensive Two-Dimensional Gas Chromatography in Environmental Analysis. *TrAC - Trends Anal. Chem.* **2018**, *106*, 225–245. https://doi.org/10.1016/j.trac.2018.07.001.

(10) Wang, D. K. W.; Austin, C. C. Determination of Complex Mixtures of Volatile Organic Compounds in Ambient Air: An Overview. *Anal. Bioanal. Chem.* **2006**, *386* (4), 1089–1098. https://doi.org/10.1007/s00216-006-0475-5.

(11) Forbes, P. B. C.; Garland, R. M. *Outdoor Air Pollution*; Elsevier Ltd, 2016; Vol. 73.

https://doi.org/10.1016/bs.coac.2016.02.004.

(12) Evuti, A. M. A Synopsis on Biogenic and Anthropogenic Volatile Organic Compounds Emissions: Hazards and Control. *Int. J. Eng. Sci.* **2013**, *2* (5), 145–153.

(13) Raza, N.; Hashemi, B.; Kim, K. H.; Lee, S. H.; Deep, A. Aromatic Hydrocarbons in Air, Water, and Soil: Sampling and Pretreatment Techniques. *TrAC - Trends Anal. Chem.* **2018**, *103*, 56–73. https://doi.org/10.1016/j.trac.2018.03.012.

(14) Hamilton, J. F.; Lewis, A. C. Comprehensive Two-Dimensional Gas Chromatography. In *Volatile Organic Compounds in the Atmosphere*; Blackwell Publishing Ltd, 2007; pp 468–488.

(15) Weitekamp, C. A.; Stevens, T.; Stewart, M. J.; Bhave, P.; Gilmour, M. I. Health Effects from Freshly Emitted versus Oxidatively or Photochemically Aged Air Pollutants. *Sci. Total Environ.* **2020**, *704*, 135772. https://doi.org/10.1016/j.scitotenv.2019.135772.

(16) Król, S.; Zabiegała, B.; Namieśnik, J. Monitoring and Analytics of Semivolatile Organic Compounds (SVOCs) in Indoor Air. *Anal. Bioanal. Chem.* **2011**, *400* (6), 1751–1769. https://doi.org/10.1007/s00216-011-4910-x.

(17) Woolfenden, E. A.; McClenny, W. A. Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes. *Compend. Methods Determ. Toxic Org. Compd. Ambient Air* **1999**, 53.

(18) McClenny, W. A.; Holdren, M. W. Determination Of Volatile Organic Compounds (VOCs) In Ambient Air Using Specially Prepared Canisters With Subsequent Analysis By Gas Chromatography/ Mass Spectrometry (GC/MS). *Compend. Methods Determ. Toxic Org. Compd. Ambient Air* **1999**, 63.

(19) Hoh, E.; Dodder, N. G.; Lehotay, S. J.; Pangallo, K. C.; Reddy, C. M.; Maruya, K. A. Nontargeted Comprehensive Two-Dimensional Gas Chromatography/Time-of-Flight Mass Spectrometry Method and Software for Inventorying Persistent and Bioaccumulative Contaminants in Marine Environments. *Environ. Sci. Technol.* **2012**, *46* (15), 8001–8008. https://doi.org/10.1021/es301139q.

(20) Llewellyn, G. T.; Dorman, F.; Westland, J. L.; Yoxtheimer, D.; Grieve, P.; Sowers, T.;

Humston-Fulmer, E.; Brantley, S. L. Evaluating a Groundwater Supply Contamination Incident Attributed to Marcellus Shale Gas Development. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112* (20), 6325–6330. https://doi.org/10.1073/pnas.1420279112.

(21) Dévier, M. H.; Mazellier, P.; Aït-Aïssa, S.; Budzinski, H. New Challenges in Environmental Analytical Chemistry: Identification of Toxic Compounds in Complex Mixtures. *Comptes Rendus Chim.* **2011**, *14* (7–8), 766–779. https://doi.org/10.1016/j.crci.2011.04.006.

(22) Pani, O.; Górecki, T. Comprehensive Two-Dimensional Gas Chromatography (GC×GC) in Environmental Analysis and Monitoring. *Anal. Bioanal. Chem.* **2006**, *386* (4), 1013–1023. https://doi.org/10.1007/s00216-006-0568-1.

(23) Hamilton, J. F.; Lewis, A. C. Monoaromatic Complexity in Urban Air and Gasoline Assessed Using Comprehensive GC and Fast GC-TOF/MS. *Atmos. Environ.* **2003**, *37* (5), 589–602. https://doi.org/10.1016/S1352-2310(02)00930-5.

(24) Aragón, P.; Atienza, J.; Climent, M. D. *Analysis of Organic Compounds in Air: A Review*; 2000; Vol. 30. https://doi.org/10.1080/10408340091164207.

(25) Marć, M.; Tobiszewski, M.; Zabiegała, B.; Guardia, M. de la; Namieśnik, J. Current Air Quality Analytics and Monitoring: A Review. *Analytica Chimica Acta*. 2015, pp 116–126. https://doi.org/10.1016/j.aca.2014.10.018.

(26) Santos, F. J.; Galceran, M. T. The Application of Gas Chromatography to Environmental Analysis. *TrAC - Trends Anal. Chem.* **2002**, *21* (9–10), 672–685. https://doi.org/10.1016/S0165-9936(02)00813-0.

(27) Vogt, L.; Gröger, T.; Zimmermann, R. Automated Compound Classification for Ambient Aerosol Sample Separations Using Comprehensive Two-Dimensional Gas Chromatography-Time-of-Flight Mass Spectrometry. *J. Chromatogr. A* **2007**, *1150* (1–2), 2–12. https://doi.org/10.1016/j.chroma.2007.03.006.

(28) CDC - NIOSH Pocket Guide to Chemical Hazards - Dichlorodifluoromethane https://www.cdc.gov/niosh/npg/npgd0192.html (accessed Oct 5, 2021).

(29) Methylene Chloride | NIOSH | CDC

https://www.cdc.gov/niosh/topics/methylenechloride/default.html (accessed Sep 5, 2021).

(30) Methyl Iodide (Iodomethane) Hazard Summary https://www.epa.gov/sites/production/files/2016-09/documents/methyl-iodide.pdf.

(31) Carbon disulfide https://www.epa.gov/sites/default/files/2016-09/documents/carbon-disulfide.pdf. https://doi.org/10.1016/B0-12-369400-0/00183-6.

(32) Methyl ethyl ketone: (Butanone) https://www.epa.gov/sites/default/files/2016-09/documents/methyl-ethyl-ketone.pdf. https://doi.org/10.1080/00968205709343470.

(33) Methyl methacrylate https://www.epa.gov/sites/default/files/2016-09/documents/methyl-methacrylate.pdf. https://doi.org/10.1201/b10505-118.

(34) CDC - NIOSH Pocket Guide to Chemical Hazards - Dichlorotetrafluoroethane https://www.cdc.gov/niosh/npg/npgd0201.html (accessed Oct 5, 2021).

(35) US.EPA. Vinyl Chloride - Hazard summary https://19january2017snapshot.epa.gov/sites/production/files/2016-09/documents/vinyl-chloride.pdf.

(36) Methyl Bromide (Bromomethane) https://www.epa.gov/sites/default/files/2016-09/documents/methyl-bromide.pdf.

(37) Environmental Protection Agency. Ethyl chloride (Chloroethane) https://www.epa.gov/sites/default/files/2016-09/documents/ethyl-chloride.pdf.

(38) CDC - NIOSH Pocket Guide to Chemical Hazards - Fluorotrichloromethane https://www.cdc.gov/niosh/npg/npgd0290.html (accessed Oct 5, 2021).

(39) EPA. 1,1-dichloroethene https://www.epa.gov/sites/production/files/2016-09/documents/2-4-6-trichlorophenol.pdf%0Ahttp://www.gascape.org/index_02/pcbepa.html.

(40) Methyl Chloride (Chloromethane) https://www.epa.gov/sites/default/files/2016-09/documents/methyl-chloride.pdf.

(41) 1-Propene, 3-chloro- (3-Chloropropene) - Canada.ca https://www.canada.ca/en/health-canada/services/chemical-substances/challenge/batch-6/3-chloropropene.html (accessed

Oct 5, 2021).

(42) Request for Assistance in Preventing Death from Excessive Exposure to Chlorofluorocarbon 113 (CFC-113). **2020**. https://doi.org/10.26616/NIOSHPUB89109.

(43) US Environmental Protection Agency. Ethylidene Dichloride (1,1-Dichloroethane) https://nj.gov/health/eoh/rtkweb/documents/fs/1211.pdf%0Ahttp://www.gascape.org/index_02/pcbepa.html.

(44) 1,1,1-Trichloroethane | Medical Management Guidelines | Toxic Substance Portal | ATSDR https://wwwn.cdc.gov/TSP/MMG/MMGDetails.aspx?mmgid=427&toxid=76 (accessed Oct 5, 2021).

(45) CDC | Facts About Benzene https://emergency.cdc.gov/agent/benzene/basics/facts.asp (accessed Apr 10, 2020).

(46) Carbon Tetrachloride Toxicity: What Are the Toxicological Effects of Carbon Tetrachloride Exposure? | Environmental Medicine | ATSDR https://www.atsdr.cdc.gov/csem/carbon-tetrachloride/toxicological_effects.html (accessed Oct 5, 2021).

(47) CDC - NIOSH Pocket Guide to Chemical Hazards - Propylene dichloride https://www.cdc.gov/niosh/npg/npgd0534.html (accessed Oct 5, 2021).

(48) Trichloroethylene | NIOSH | CDC https://www.cdc.gov/niosh/topics/trichloroethylene/default.html (accessed Sep 5, 2021).

(49) CDC - NIOSH Pocket Guide to Chemical Hazards - 1,3-Dichloropropene https://www.cdc.gov/niosh/npg/npgd0199.html (accessed Sep 5, 2021).

(50) 1,1,2-Trichloroethane https://www.epa.gov/sites/default/files/2016-09/documents/1-1-2-trichloroethane.pdf. https://doi.org/10.1002/9780470114735.hawley16322.

(51) Methyl isobutyl ketone (Hexone) https://www.epa.gov/sites/default/files/2016-09/documents/methyl-isobutyl-ketone.pdf.

(52) Toluene | NIOSH | CDC https://www.cdc.gov/niosh/topics/toluene/default.html (accessed Sep 5, 2021).

(53) CDC - NIOSH Pocket Guide to Chemical Hazards - Ethylene dibromide https://www.cdc.gov/niosh/npg/npgd0270.html (accessed Oct 5, 2021).

(54) Tetrachloroethylene (perchloroethylene) https://www.epa.gov/sites/default/files/2016-09/documents/tetrachloroethylene.pdf. https://doi.org/10.1080/0002889778507753.

(55) 2-Hexanone - ToxFAQs https://www.atsdr.cdc.gov/toxfaqs/tfacts44.pdf.

(56) CDC - NIOSH Pocket Guide to Chemical Hazards - Chlorobenzene https://www.cdc.gov/niosh/npg/npgd0121.html (accessed Oct 5, 2021).

(57) Ethylbenzene https://www.epa.gov/sites/default/files/2016-09/documents/ethylbenzene.pdf.

(58) Xylene | NIOSH | CDC https://www.cdc.gov/niosh/topics/xylene/default.html (accessed Sep 5, 2021).

(59) Styrene https://19january2017snapshot.epa.gov/sites/production/files/2016-09/documents/styrene.pdf.

(60) 1,1,2,2-tetrachloroethane https://www.epa.gov/sites/default/files/2016-09/documents/1-1-2-2-tetrachloroethane.pd.

(61) Substance Information - ECHA https://echa.europa.eu/substance-information/-/substanceinfo/100.009.784?_disssubsinfo_WAR_disssubsinfoportlet_backURL=https%3A%2F%2Fecha.europa.eu%2Fhome%3Fp_p_id%3Ddisssimplesearchhomepage_WAR_disssearchportlet%26p_p_lifecycle%3D0%26p_p_state%3Dnormal%26p_p_mode%3Dview%26_disssimplesearchhomepage_WAR_disssearchportlet_sessionCriteriaId%3D (accessed Oct 5, 2021).

(62) CDC - NIOSH Pocket Guide to Chemical Hazards - 1,3,5-Trimethylbenzene https://www.cdc.gov/niosh/npg/npgd0639.html (accessed Oct 5, 2021).

(63) CDC - NIOSH Pocket Guide to Chemical Hazards - 1,2,4-Trimethylbenzene https://www.cdc.gov/niosh/npg/npgd0638.html (accessed Oct 5, 2021).

(64) Dichlorobenzenes | ToxFAQs^{TM} | ATSDR https://wwwn.cdc.gov/TSP/ToxFAQs/ToxFAQsDetails.aspx?faqid=703&toxid=126

(accessed Oct 5, 2021).

(65) CDC - NIOSH Pocket Guide to Chemical Hazards - Benzyl chloride https://www.cdc.gov/niosh/npg/npgd0053.html (accessed Oct 5, 2021).

(66) 1,4-Dichlorobenzene (para-Dichlorobenzene) https://www.epa.gov/sites/default/files/2016-09/documents/1-4-dichlorobenzene.pdf.

(67) CDC - NIOSH Pocket Guide to Chemical Hazards - o-Dichlorobenzene https://www.cdc.gov/niosh/npg/npgd0189.html (accessed Oct 5, 2021).

(68) Cumene https://www.epa.gov/sites/default/files/2016-09/documents/cumene.pdf.

(69) 1,2-Dibromo-3-chloropropane https://www.epa.gov/sites/default/files/2016-09/documents/1-2-dibromo-3-chloropropane.pdf.

(70) Hexachloroethane https://www.epa.gov/sites/default/files/2016-09/documents/hexachloroethane.pdf.

(71) Nitrobenzene https://www.epa.gov/sites/default/files/2016-09/documents/nitrobenzene.pdf.

(72) 1,2,4-trichlorobenzene https://www.epa.gov/sites/default/files/2016-09/documents/1-2-4-trichlorobenzene.pdf.

(73) Hexachlorobutadiene https://www.epa.gov/sites/default/files/2016-09/documents/hexachlorobutadeine.pdf. https://doi.org/10.1201/9781420009132-217.

(74) Camel, V.; Caude, M. Trace Enrichment Methods for the Determination of Organic Pollutants in Ambient Air. *J. Chromatogr. A* **1995**, *710* (1), 3–19. https://doi.org/10.1016/0021-9673(95)00080-7.

(75) Lenine, R. How Air Pollution Is Destroying Our Health. *World Heal. Organ.* **2016**, 4.

(76) Williams, J.; Koppmann, R. Volatile Organic Compounds in the Atmosphere. In *Volatile Organic Compounds in the Atmosphere*; Blackwell Publishing Ltd, 2007; pp 1–32. https://doi.org/10.1002/9780470988657.

(77) Rumchev, K.; Brown, H.; Spickett, J. Volatile Organic Compounds: Do They Present a

Risk to Our Health? *Rev. Environ. Health* **2007**, *22* (1), 39–55. https://doi.org/10.1515/REVEH.2007.22.1.39.

(78) EPA. What are Hazardous Air Pollutants? https://www.epa.gov/haps/what-are-hazardous-air-pollutants (accessed Apr 13, 2020).

(79) Strandberg, B.; Sunesson, A. L.; Olsson, K.; Levin, J. O.; Ljungqvist, G.; Sundgren, M.; Sällsten, G.; Barregard, L. Evaluation of Two Types of Diffusive Samplers and Adsorbents for Measuring 1,3-Butadiene and Benzene in Air. *Atmos. Environ.* **2005**, *39* (22), 4101–4110. https://doi.org/10.1016/j.atmosenv.2005.03.039.

(80) Gallego, E.; Teixidor, P.; Roca, F. J.; Perales, J. F.; Gadea, E. Outdoor Air 1,3-Butadiene Monitoring: Comparison of Performance of Radiello® Passive Samplers and Active Multi-Sorbent Bed Tubes. *Atmos. Environ.* **2018**, *182*, 9–16. https://doi.org/10.1016/j.atmosenv.2018.03.022.

(81) Sakurai, K.; Miyake, Y.; Amagai, T. Reliable Passive-Sampling Method for Determining Outdoor 1,3-Butadiene Concentrations in Air. *Atmos. Environ.* **2013**, *80*, 198–203. https://doi.org/10.1016/j.atmosenv.2013.07.039.

(82) Vallecillos, L.; Sanmartin, J.; Marcé, R. M.; Borrull, F. Determination of 1,3-Butadiene Degradation Products in Air Samples by Thermal Desorption-Gas Chromatography-Mass Spectrometry. *Atmos. Environ.* **2019**, *196* (May 2018), 95–102. https://doi.org/10.1016/j.atmosenv.2018.10.010.

(83) Lebedev, A. T.; Mazur, D. M.; Artaev, V. B.; Tikhonov, G. Y. Better Screening of Non-Target Pollutants in Complex Samples Using Advanced Chromatographic and Mass Spectrometric Techniques. *Environ. Chem. Lett.* **2020**, *18* (5), 1753–1760. https://doi.org/10.1007/s10311-020-01037-2.

(84) (EPA), U. S. E. P. A. *Health and Environmental Effects of Hazardous Air Pollutants*; 2015.

(85) Thron, R. W. Direct and Indirect Exposure to Air Pollution. *Otolaryngol. - Head Neck Surg.* **1996**, *114* (2), 281–285. https://doi.org/10.1016/S0194-5998(96)70184-5.

(86) Ground-level Ozone Basics | Ground-level Ozone Pollution | US EPA

https://www.epa.gov/ground-level-ozone-pollution/ground-level-ozone-basics (accessed Jan 12, 2021).

(87) Dewulf, J.; Van Langenhove, H.; Wittmann, G. Analysis of Volatile Organic Compounds Using Gas Chromatography. *Trends Anal. Chem.* **2002**, *21*, 637–646.

(88) Health Effects of Ozone Pollution | Ground-level Ozone Pollution | US EPA https://www.epa.gov/ground-level-ozone-pollution/health-effects-ozone-pollution (accessed Jan 12, 2021).

(89) Ecosystem Effects of Ozone Pollution | Ground-level Ozone Pollution | US EPA https://www.epa.gov/ground-level-ozone-pollution/ecosystem-effects-ozone-pollution (accessed Jan 12, 2021).

(90) Woolfenden, E. Sorbent-Based Sampling Methods for Volatile and Semi-Volatile Organic Compounds in Air. Part 1: Sorbent-Based Air Monitoring Options. *J. Chromatogr. A* **2010**, *1217* (16), 2674–2684. https://doi.org/10.1016/j.chroma.2009.12.042.

(91) Colman Lerner, J. E.; Orte, M. A.; Giuliani, D.; Matamoros, N.; Sanchez, E. Y.; Porta, A. A. *Volatile and Semivolatile Organic Compounds Determination in Air*; Elsevier Ltd, 2016; Vol. 73. https://doi.org/10.1016/bs.coac.2016.02.009.

(92) Marć, M.; Namieśnik, J.; Zabiegała, B. Active Sampling of Air. *Compr. Anal. Chem.* **2016**, *73*, 167–201. https://doi.org/10.1016/bs.coac.2016.02.006.

(93) Woolfenden, E. Sorbent-Based Sampling Methods for Volatile and Semi-Volatile Organic Compounds in Air. Part 2. Sorbent Selection and Other Aspects of Optimizing Air Monitoring Methods. *J. Chromatogr. A* **2010**, *1217* (16), 2685–2694. https://doi.org/10.1016/j.chroma.2010.01.015.

(94) Woolfenden, E. Thermal Desorption for Gas Chromatography. In *Gas Chromatography*; Elsevier Inc., 2012; pp 235–289. https://doi.org/10.1016/B978-0-12-385540-4.00010-9.

(95) Król, S.; Zabiegała, B.; Namieśnik, J. Monitoring VOCs in Atmospheric Air II. Sample Collection and Preparation. *TrAC - Trends Anal. Chem.* **2010**, *29* (9), 1101–1112. https://doi.org/10.1016/j.trac.2010.05.010.

(96) Ras, M. R.; Borrull, F.; Marcé, R. M. Sampling and Preconcentration Techniques for Determination of Volatile Organic Compounds in Air Samples. *TrAC - Trends Anal. Chem.* **2009**, *28* (3), 347–361. https://doi.org/10.1016/j.trac.2008.10.009.

(97) TO-Can Air Sampling Canisters with Swagelok SS4H Bellows Valve https://www.restek.com/row/products/sample-preparation--air-sampling/air-gas-sampling-products/volatile-organic-compound-voc-sampling/45330/ (accessed Jan 6, 2022).

(98) Tedlar Sampling Bags https://www.restek.com/row/products/sample-preparation--air-sampling/air-gas-sampling-products/volatile-organic-compound-voc-sampling/3795/ (accessed Jan 6, 2022).

(99) Seethapathy, S.; Górecki, T.; Li, X. Passive Sampling in Environmental Analysis. *J. Chromatogr. A* **2008**, *1184* (1–2), 234–253. https://doi.org/10.1016/j.chroma.2007.07.070.

(100) Harper, M. Sorbent Trapping of Volatile Organic Compounds from Air. *J. Chromatogr. A* **2000**, *885* (1–2), 129–151. https://doi.org/10.1016/S0021-9673(00)00363-0.

(101) Ramírez, N.; Cuadras, A.; Rovira, E.; Borrull, F.; Marcé, R. M. Comparative Study of Solvent Extraction and Thermal Desorption Methods for Determining a Wide Range of Volatile Organic Compounds in Ambient Air. *Talanta* **2010**, *82* (2), 719–727. https://doi.org/10.1016/j.talanta.2010.05.038.

(102) Markes International. User Manual. 2018.

(103) Brown, R. .; Purnell, C. . Collection and Analysis of Trace Organic Vapour Pollutants in Ambient Atmospheres : The Performace of a Tenax-GC Adsorbent Tube. *J. Chromatogr. A* **1979**, *178* (1), 79–90.

(104) Coker, D. T.; Van Den Hoed, N.; Saunders, K. J.; Tindle, P. E. A Monitoring Method for Gasoline Vapour Giving Detailed Composition. *Ann. Occup. Hyg.* **1989**, *33* (1), 15–26. https://doi.org/10.1093/annhyg/33.1.15.

(105) Woolfenden, E. A. Monitoring VOCs in Air Using Sorbent Tubes Followed by Thermal Desorption-Capillary GC Analysis: Summary of Data and Practical Guidelines. *J. Air Waste Manag. Assoc.* **1997**, *47* (1), 20–36. https://doi.org/10.1080/10473289.1997.10464411.

(106) Kim, Y. H.; Kim, K. H. Critical Role of a Pre-Purge Setup in the Thermal Desorption Analysis of Volatile Organic Compounds by Gas Chromatography with Mass Spectrometry. *J. Sep. Sci.* **2015**, *38* (14), 2455–2462. https://doi.org/10.1002/jssc.201500367.

(107) Heavner, D. L.; Ogden, M. W.; Nelson, P. R. Multisorbent Thermal Desorption/Gas Chromatography/Mass Selective Detection Method for the Determination of Target Volatile Organic Compounds in Indoor Air. *Environ. Sci. Technol.* **1992**, *26* (9), 1737–1746. https://doi.org/10.1021/es00033a004.

(108) Hassoun, S.; Pilling, M. J.; Bartle, K. D. A Catalogue of Urban Hydrocarbons for the City of Leeds: Atmospheric Monitoring of Volatile Organic Compounds by Thermal Desorption-Gas Chromatography. *J. Environ. Monit.* **1999**, *1* (5), 453–458. https://doi.org/10.1039/a904879k.

(109) Pankow, J. F.; Luo, W.; Isabelle, L. M.; Bender, D. A.; Baker, R. J. Determination of a Wide Range of Volatile Organic Compounds in Ambient Air Using Multisorbent Adsorption/Thermal Desorption and Gas Chromatography/Mass Spectrometry. *Anal. Chem.* **1998**, *70* (24), 5213–5221. https://doi.org/10.1021/ac980481t.

(110) Wang, B.; Sivret, E. C.; Parcsi, G.; Stuetz, R. M. Determination of VOSCs in Sewer Headspace Air Using TD-GC-SCD. *Talanta* **2015**, *137*, 71–79. https://doi.org/10.1016/j.talanta.2014.11.072.

(111) Veenaas, C.; Ripszam, M.; Haglund, P. Analysis of Volatile Organic Compounds in Indoor Environments Using Thermal Desorption with Comprehensive Two-dimensional Gas Chromatography and High-resolution Time-of-flight Mass Spectrometry. *J. Sep. Sci.* **2020**, 1–10. https://doi.org/10.1002/jssc.201901103.

(112) Veenaas, C.; Ripszam, M.; Glas, B.; Liljelind, I.; Claeson, A. S.; Haglund, P. Differences in Chemical Composition of Indoor Air in Rooms Associated/Not Associated with Building Related Symptoms. *Sci. Total Environ.* **2020**, *720*, 137444. https://doi.org/10.1016/j.scitotenv.2020.137444.

(113) Kumar, A.; Víden, I. Volatile Organic Compounds: Sampling Methods and Their

Worldwide Profile in Ambient Air. *Environ. Monit. Assess.* **2007**, *131* (1–3), 301–321. https://doi.org/10.1007/s10661-006-9477-1.

(114) Dettmer, K.; Engewald, W. Adsorbent Materials Commonly Used in Air Analysis for Adsorptive Enrichment and Thermal Desorption of Volatile Organic Compounds. *Anal. Bioanal. Chem.* **2002**, *373* (6), 490–500. https://doi.org/10.1007/s00216-002-1352-5.

(115) Ribes, A.; Carrera, G.; Gallego, E.; Roca, X.; Berenguer, M. J.; Guardino, X. Development and Validation of a Method for Air-Quality and Nuisance Odors Monitoring of Volatile Organic Compounds Using Multi-Sorbent Adsorption and Gas Chromatography/Mass Spectrometry Thermal Desorption System. *J. Chromatogr. A* **2007**, *1140* (1–2), 44–55. https://doi.org/10.1016/j.chroma.2006.11.062.

(116) Dettmer, K.; Engewald, W. Ambient Air Analysis of Volatile Organic Compounds Using Adsorptive Enrichment. *Chromatographia* **2003**, *57* (SUPPL.), 339–347. https://doi.org/10.1007/BF02492126.

(117) Górecki, T.; Harynuk, J.; Panić, O. The Evolution of Comprehensive Two-Dimensional Gas Chromatography (GC x GC). *J. Sep. Sci.* **2004**, *27* (5–6), 359–379. https://doi.org/10.1002/jssc.200301650.

(118) Galceran, M. T.; Santos, F. J.; Snow, N. H. Gas Chromatography | Environmental Applications. *Encycl. Anal. Sci.* **2019**, *4* (July 2018), 148–157. https://doi.org/10.1016/B978-0-12-409547-2.14472-5.

(119) Sanz, J. Theoretical Considerations. In *Comprehensive Analytical Chemistry*; Elsevier, 2009; Vol. 55, pp 49–76. https://doi.org/10.1016/S0166-526X(09)05503-2.

(120) Hinshaw, J. V. A Compendium of GC Terms and Techniques. *LC GC Eur.* **2003**, *16* (3), 140–146.

(121) Poole, C. F. *Classification and Selection of Open-Tubular Columns for Analytical Separations*; Elsevier Inc., 2012. https://doi.org/10.1016/B978-0-12-385540-4.00006-7.

(122) Dorman, F. L.; Dawes, P. Column Technology: Open Tubular Columns. In *Gas Chromatography*; Elsevier Inc., 2012; pp 79–96. https://doi.org/10.1016/B978-0-12-385540-4.00003-1.

(123) D. Bartle, K.; Myers, P. History of Gas Chromatography. *Trends Anal. Chem.* **2002**, *21* (9+10), 547–557. https://doi.org/10.1038/1661000b0.

(124) Klee, M. S. *Detectors*; Elsevier Inc., 2012. https://doi.org/10.1016/B978-0-12-385540-4.00012-2.

(125) Seeley, J. V. Multidimensional and Comprehensive Gas Chromatography. In *Gas Chromatography*; Elsevier Inc., 2012; pp 161–185. https://doi.org/10.1016/B978-0-12-385540-4.00007-9.

(126) Ballesteros-Gómez, A.; Rubio, S. Recent Advances in Environmental Analysis. *Anal. Chem.* **2011**, *83*, 4579–4613. https://doi.org/10.1021/ac200921j.

(127) Ramos, J. J.; Pena-abaurrea, M.; Ramos, L. Environmental Analysis. In *Comprehensive Analytical Chemistry*; Elsevier Inc., 2009; Vol. 55, pp 243–280. https://doi.org/10.1016/S0166-526X(09)05511-1.

(128) Marcé, R. M. Multidimensional Chromatography in Environmental Analysis. In *Multidimensional Chromatography*; 2002; Vol. 3, pp 335–377.

(129) Giddings, J. C. Two-Dimensional Separations: Concept and Promise. *Anal. Chem.* **1984**, *56* (12). https://doi.org/10.1021/ac00276a003.

(130) Liu, Z.; Phillips, J. B. Comprehensive Two-Dimensional Gas Chromatography Using an on-Column Thermal Modulator Interface. *J. Chromatogr. Sci.* **1991**, *29* (5), 227–231. https://doi.org/10.1093/chromsci/29.6.227.

(131) Tranchida, P. Q.; Franchina, F. A.; Dugo, P.; Mondello, L. Comprehensive Two-Dimensional Gas Chromatography-Mass Spectrometry: Recent Evolution and Current Trends. *Mass Spectrom. Rev.* **2016**, *35*, 524–534. https://doi.org/10.1002/mas.

(132) Stefanuto, P. H.; Focant, J. F. Columns and Column Configurations. In *Separation Science and Technology (New York)*; 2020; Vol. 12, pp 69–88. https://doi.org/10.1016/B978-0-12-813745-1.00003-9.

(133) Tranchida, P. Q.; Purcaro, G.; Dugo, P.; Mondello, L.; Purcaro, G. Modulators for Comprehensive Two-Dimensional Gas Chromatography. *TrAC - Trends Anal. Chem.*

2011, *30* (9), 1437–1461. https://doi.org/10.1016/j.trac.2011.06.010.

(134) Prebihalo, S. E.; Berrier, K. L.; Freye, C. E.; Bahaghighat, H. D.; Moore, N. R.; Pinkerton, D. K.; Synovec, R. E. Multidimensional Gas Chromatography: Advances in Instrumentation, Chemometrics, and Applications. *Anal. Chem.* **2018**, *90* (1), 505–532. https://doi.org/10.1021/acs.analchem.7b04226.

(135) Bahaghighat, H. D.; Freye, C. E.; Synovec, R. E. Recent Advances in Modulator Technology for Comprehensive Two Dimensional Gas Chromatography. *TrAC - Trends Anal. Chem.* **2019**, *113*, 379–391. https://doi.org/10.1016/j.trac.2018.04.016.

(136) Boswell, H.; Chow, H. Y.; Górecki, T. *Modulators*; Elsevier, 2020; Vol. 12. https://doi.org/10.1016/B978-0-12-813745-1.00004-0.

(137) Stilo, F.; Gabetti, E.; Bicchi, C.; Carretta, A.; Peroni, D.; Reichenbach, S. E.; Cordero, C.; McCurry, J. A Step Forward in the Equivalence between Thermal and Differential-Flow Modulated Comprehensive Two-Dimensional Gas Chromatography Methods. *J. Chromatogr. A* **2020**, *1627*, 461396. https://doi.org/10.1016/j.chroma.2020.461396.

(138) Gaines, R. B.; Frysinger, G. S.; Hendrick-Smith, M. S.; Stuart, J. D. Oil Spill Source Identification by Comprehensive Two-Dimensional Gas Chromatography. *Environ. Sci. Technol.* **1999**, *33* (12), 2106–2112. https://doi.org/10.1021/es9810484.

(139) Beens, J.; Dallüge, J.; Adahchour, M.; Vreuls, R. J. J.; Brinkman, U. A. T. Moving Cryogenic Modulator for the Comprehensive Two-Dimensional Gas Chromatography (GC X GC) of Surface Water Contaminants. *J. Microcolumn Sep.* **2001**, *13* (3), 134–140. https://doi.org/10.1002/mcs.1030.

(140) Lewis, A. C.; Carslaw, N.; Marriott, P. J.; Kinghorn, R. M.; Morrison, P.; Lee, A. L.; Bartie, K. D.; Pilling, M. J. A Larger Pool of Ozone-Forming Carbon Compounds in Urban Atmospheres. *Nature* **2000**, *405* (6788), 778–781. https://doi.org/10.1038/35015540.

(141) Kallio, M.; Hyötyläinen, T.; Lehtonen, M.; Jussila, M.; Hartonen, K.; Shimmo, M.; Riekkola, M. L. Comprehensive Two-Dimensional Gas Chromatography in the Analysis of Urban Aerosols. *J. Chromatogr. A* **2003**, *1019* (1–2), 251–260.

https://doi.org/10.1016/S0021-9673(03)01238-X.

(142) Xu, T.; Lv, Y.; Cheng, T.; Li, X. Using Comprehensive GC × GC to Study PAHs and N-Alkanes Associated with PM2.5 in Urban Atmosphere. *Environ. Sci. Pollut. Res.* **2015**, *22*, 5253–5262. https://doi.org/10.1007/s11356-014-3695-9.

(143) Goldstein, A. H.; Worton, D. R.; Williams, B. J.; Hering, S. V.; Kreisberg, N. M.; Panić, O.; Górecki, T. Thermal Desorption Comprehensive Two-Dimensional Gas Chromatography for in-Situ Measurements of Organic Aerosols. *J. Chromatogr. A* **2008**, *1186* (1–2), 340–347. https://doi.org/10.1016/j.chroma.2007.09.094.

(144) Worton, D. R.; Kreisberg, N. M.; Isaacman, G.; Teng, A. P.; McNeish, C.; Górecki, T.; Hering, S. V.; Goldstein, A. H. Thermal Desorption Comprehensive Two-Dimensional Gas Chromatography: An Improved Instrument for in-Situ Speciated Measurements of Organic Aerosols. *Aerosol Sci. Technol.* **2012**, *46* (4), 380–393. https://doi.org/10.1080/02786826.2011.634452.

(145) Hoh, E.; Lehotay, S. J.; Mastovska, K.; Ngo, H. L.; Vetter, W.; Pangallo, K. C.; Reddy, C. M. Capabilities of Direct Sample Introduction-Comprehensive Two-Dimensional Gas Chromatography-Time-of-Flight Mass Spectrometry to Analyze Organic Chemicals of Interest in Fish Oils. *Environ. Sci. Technol.* **2009**, *43* (9), 3240–3247. https://doi.org/10.1021/es803486x.

(146) Murray, J. A. Qualitative and Quantitative Approaches in Comprehensive Two-Dimensional Gas Chromatography. *J. Chromatogr. A* **2012**, *1261*, 58–68. https://doi.org/10.1016/j.chroma.2012.05.012.

(147) Cordero, C.; Liberto, E.; Bicchi, C.; Rubiolo, P.; Reichenbach, S. E.; Tian, X.; Tao, Q. Targeted and Non-Targeted Approaches for Complex Natural Sample Profiling by GC×GC-QMS. *J. Chromatogr. Sci.* **2010**, *48* (4), 251–261. https://doi.org/10.1093/chromsci/48.4.251.

(148) Manzano, C. A.; Dodder, N. G.; Hoh, E.; Morales, R. Patterns of Personal Exposure to Urban Pollutants Using Personal Passive Samplers and GC × GC/ToF–MS. *Environ. Sci. Technol.* **2019**, *53* (2), 614–624. https://doi.org/10.1021/acs.est.8b06220.

(149) Gallego, E.; Roca, F. J.; Perales, J. F.; Guardino, X. Comparative Study of the Adsorption Performance of a Multi-Sorbent Bed (Carbotrap, Carbopack X, Carboxen 569) and a Tenax TA Adsorbent Tube for the Analysis of Volatile Organic Compounds (VOCs). *Talanta* **2010**, *81* (3), 916–924. https://doi.org/10.1016/j.talanta.2010.01.037.

(150) Wood, L. Insight Flow Modulator User Guide. **2017**, *44* (August), 1–12.

(151) Murphy, R. E.; Schure, M. R.; Foley, J. P. Effect of Sampling Rate on Resolution in Comprehensive Two-Dimensional Liquid Chromatography. *Anal. Chem.* **1998**, *70* (8), 1585–1594. https://doi.org/10.1021/ac971184b.

(152) Khummueng, W.; Harynuk, J.; Marriott, P. J. Modulation Ratio in Comprehensive Two-Dimensional Gas Chromatography. *Anal. Chem.* **2006**, *78* (13), 4578–4587. https://doi.org/10.1021/ac052270b.

(153) Markes International. Application Note 086 Automated Cryogen-Free Monitoring of ‘ Air Toxics ’ in Ambient Air Using TD – GC – MS in Accordance with US EPA Method TO - 17. **2019**, No. May.

(154) Ramírez, N.; Marcé, R. M.; Borrull, F. Determination of Volatile Organic Compounds in Industrial Wastewater Plant Air Emissions by Multi-Sorbent Adsorption and Thermal Desorption-Gas Chromatography-Mass Spectrometry. *Int. J. Environ. Anal. Chem.* **2011**, *91* (10), 911–928. https://doi.org/10.1080/03067310903584073.

(155) Markes International. Application Note 021 Developing and Optimising Tube-Based Thermal Desorption Methods. **2019**, *44* (April 2014).

(156) Wong, G. K. S.; Ng, S. J.; Webster, R. D. Quantitative Analysis of Atmospheric Volatile Organic Pollutants by Thermal Desorption Gas Chromatography Mass Spectrometry. *Anal. Methods* **2013**, *5* (1), 219–230. https://doi.org/10.1039/c2ay25982f.

(157) Marcillo, A.; Jakimovska, V.; Widdig, A.; Birkemeyer, C. Comparison of Two Common Adsorption Materials for Thermal Desorption Gas Chromatography – Mass Spectrometry of Biogenic Volatile Organic Compounds. *J. Chromatogr. A* **2017**, *1514*, 16–28. https://doi.org/10.1016/j.chroma.2017.07.005.

(158) Faiola, C. L.; Erickson, M. H.; Fricaud, V. L.; Jobson, B. T.; Vanreken, T. M.

Quantification of Biogenic Volatile Organic Compounds with a Flame Ionization Detector Using the Effective Carbon Number Concept. *Atmos. Meas. Tech.* **2012**, *5* (8), 1911–1923. https://doi.org/10.5194/amt-5-1911-2012.

(159) Karpe, P.; Kirchner, S.; Rouxel, P. Thermal Desorption-Gas Chromatography-Mass Spectrometry-Flame Ionization Detection-Sniffer Multi-Coupling: A Device for the Determination of Odorous Volatile Organic Compounds in Air. *J. Chromatogr. A* **1995**, *708* (1), 105–114. https://doi.org/10.1016/0021-9673(95)00383-X.

(160) CDC - NIOSH Pocket Guide to Chemical Hazards - Nonane https://www.cdc.gov/niosh/npg/npgd0466.html (accessed Oct 18, 2021).

(161) Brown, V. M.; Crump, D. R.; Plant, N. T.; Pengelly, I. Evaluation of the Stability of a Mixture of Volatile Organic Compounds on Sorbents for the Determination of Emissions from Indoor Materials and Products Using Thermal Desorption/Gas Chromatography/Mass Spectrometry. *J. Chromatogr. A* **2014**, *1350*, 1–9. https://doi.org/10.1016/j.chroma.2014.05.011.

(162) Ho, S. S. H.; Wang, L.; Chow, J. C.; Watson, J. G.; Xue, Y.; Huang, Y.; Qu, L.; Li, B.; Dai, W.; Li, L.; et al. Optimization and Evaluation of Multi-Bed Adsorbent Tube Method in Collection of Volatile Organic Compounds. *Atmos. Res.* **2018**, *202* (December 2017), 187–195. https://doi.org/10.1016/j.atmosres.2017.11.026.

(163) Sanchez, J. M. Air and Breath Analysis for the Assessment of Exposure to Solvent Emissions in University Chemistry Laboratories. *Atmos. Pollut. Res.* **2019**, *10* (6), 1795–1802. https://doi.org/10.1016/j.apr.2019.07.011.

(164) Healy, R. M.; Wang, J. M.; Karellas, N. S.; Todd, A.; Sofowote, U.; Su, Y.; Munoz, A. Assessment of a Passive Sampling Method and Two On-Line Gas Chromatographs for the Measurement of Benzene, Toluene, Ethylbenzene and Xylenes in Ambient Air at a Highway Site. *Atmos. Pollut. Res.* **2019**, *10* (4), 1123–1127. https://doi.org/10.1016/j.apr.2019.01.017.

(165) Wallace, L. A.; Pellizzari, E. D.; Hartwell, T. D.; Davis, V.; Michael, L. C.; Whitmore, R. W. The Influence of Personal Activities on Exposure to Volatile Organic Compounds.

Environ. Res. **1989**, *50* (1), 37–55. https://doi.org/10.1016/S0013-9351(89)80047-7.

(166) University Station - Google Maps https://www.google.ca/maps/place/University+Station/@53.5247548,-113.5219382,128m/data=!3m1!1e3!4m9!1m2!2m1!1suniversity+of+alberta+bus+station!3m5!1s0x53a0221f9ac5f811:0xbfceb9e21b8de45b!8m2!3d53.525084!4d-113.5213875!15sCiF1bml2ZXJzaXR5IG9mIGFsYmVydGEgYnVzIHN0YXRpb24iA4gBAZIBF2xvZ2ljYWxfdHJhbnNpdF9zdGF0aW9u!5m1!1e4 (accessed Jan 28, 2022).

(167) Perry, R.; Gee, I. L. Vehicle Emissions in Relation to Fuel Composition. *Sci. Total Environ.* **1995**, *169* (1–3), 149–156. https://doi.org/10.1016/0048-9697(95)04643-F.

(168) Masih, A.; Lall, A. S.; Taneja, A.; Singhvi, R. Inhalation Exposure and Related Health Risks of BTEX in Ambient Air at Different Microenvironments of a Terai Zone in North India. *Atmos. Environ.* **2016**, *147*, 55–66. https://doi.org/10.1016/j.atmosenv.2016.09.067.

(169) Esteve-Turrillas, F. A.; Pastor, A.; de la Guardia, M. Assessing Air Quality inside Vehicles and at Filling Stations by Monitoring Benzene, Toluene, Ethylbenzene and Xylenes with the Use of Semipermeable Devices. *Anal. Chim. Acta* **2007**, *593* (1), 108–116. https://doi.org/10.1016/j.aca.2007.04.055.

(170) Feng, Y.; Wen, S.; Chen, Y.; Wang, X.; Lü, H.; Bi, X.; Sheng, G.; Fu, J. Ambient Levels of Carbonyl Compounds and Their Sources in Guangzhou, China. *Atmos. Environ.* **2005**, *39* (10), 1789–1800. https://doi.org/10.1016/j.atmosenv.2004.10.009.

(171) Sagebiel, J. C.; Zielinska, B.; Pierson, W. R.; Gertler, A. W. Real-World Emissions and Calculated Reactivities of Organic Species from Motor Vehicles. *Atmos. Environ.* **1996**, *30* (12), 2287–2296. https://doi.org/10.1016/1352-2310(95)00117-4.

(172) EPA. Acetaldehyde https://www.epa.gov/sites/production/files/2016-09/documents/acetaldehyde.pdf.

(173) Li, Y.; Liu, B.; Ye, J.; Jia, T.; Khuzestani, R. B.; Sun, J. Y.; Cheng, X.; Zheng, Y.; Li, X.; Wu, C.; et al. Unmanned Aerial Vehicle Measurements of Volatile Organic Compounds over a Subtropical Forest in China and Implications for Emission Heterogeneity. *ACS Earth Sp. Chem.* **2021**, *5* (2), 247–256.

https://doi.org/10.1021/acsearthspacechem.0c00271.

(174) Marlet, C.; Lognay, G. Development and Validation by Accuracy Profile of a Method for the Analysis of Monoterpenes in Indoor Air by Active Sampling and Thermal Desorption-Gas Chromatography-Mass Spectrometry. *Talanta* **2010**, *82* (4), 1230–1239. https://doi.org/10.1016/j.talanta.2010.06.044.

(175) Mermet, K.; Sauvage, S.; Dusanter, S.; Salameh, T.; Léonardis, T.; Flaud, P. M.; Perraudin, E.; Villenave, E.; Locoge, N. Optimization of a Gas Chromatographic Unit for Measuring Biogenic Volatile Organic Compounds in Ambient Air. *Atmos. Meas. Tech.* **2019**, *12* (11), 6153–6171. https://doi.org/10.5194/amt-12-6153-2019.

(176) Churkina, G.; Kuik, F.; Bonn, B.; Lauer, A.; Grote, R.; Tomiak, K.; Butler, T. M. Effect of VOC Emissions from Vegetation on Air Quality in Berlin during a Heatwave. *Environ. Sci. Technol.* **2017**, *51* (11), 6120–6130. https://doi.org/10.1021/acs.est.6b06514.

(177) Cometto-Muñiz, J. E.; Abraham, M. H. Compilation and Analysis of Types and Concentrations of Airborne Chemicals Measured in Various Indoor and Outdoor Human Environments. *Chemosphere* **2015**, *127*, 70–86. https://doi.org/10.1016/j.chemosphere.2014.12.089.

(178) Ré-Poppi, N.; Almeida, F. F. P.; Cardoso, C. A. L.; Raposo, J. L.; Viana, L. H.; Silva, T. Q.; Souza, J. L. C.; Ferreira, V. S. Screening Analysis of Type C Brazilian Gasoline by Gas Chromatography - Flame Ionization Detector. *Fuel* **2009**, *88* (3), 418–423. https://doi.org/10.1016/j.fuel.2008.10.014.

(179) Gold Bar Parking Lot - Google Maps https://www.google.ca/maps/place/Gold+Bar+Parking+Lot/@53.5578834,-113.4071626,256m/data=!3m1!1e3!4m12!1m6!3m5!1s0x53a022cbe2786cf7:0x6293d8b14f8df8ba!2sGold+Bar+Park!8m2!3d53.5549705!4d-113.4068498!3m4!1s0x0:0x81f9c4cfe240c01a!8m2!3d53.5578674!4d-113.4073806!5m1!1e4 (accessed Jan 28, 2022).

(180) Hourly Data Report for August 04, 2021 - Climate - Environment and Climate Change Canada

https://climate.weather.gc.ca/climate_data/hourly_data_e.html?StationID=27214&timeframe=1&StartYear=1840&EndYear=2022&time=LST&time=LST&Year=2021&Month=8&Day=4# (accessed Jan 5, 2022).

(181) Hoshi, J. ya; Amano, S.; Sasaki, Y.; Korenaga, T. Investigation and Estimation of Emission Sources of 54 Volatile Organic Compounds in Ambient Air in Tokyo. *Atmos. Environ.* **2008**, *42* (10), 2383–2393. https://doi.org/10.1016/j.atmosenv.2007.12.024.

(182) Barreira, L. M. F.; Duporté, G.; Rönkkö, T.; Parshintsev, J.; Hartonen, K.; Hyrsky, L.; Heikkinen, E.; Jussila, M.; Kulmala, M.; Riekkola, M. L. Field Measurements of Biogenic Volatile Organic Compounds in the Atmosphere Using Solid-Phase Microextraction Arrow. *Atmos. Meas. Tech.* **2018**, *11* (2), 881–893. https://doi.org/10.5194/amt-11-881-2018.

(183) Mckinney, K. A.; Wang, D.; Ye, J.; Fouchier, J. B. De; Guimarães, P. C.; Batista, C. E.; Souza, R. A. F.; Alves, E. G.; Gu, D.; Guenther, A. B.; et al. A Sampler for Atmospheric Volatile Organic Compounds by Copter Unmanned Aerial Vehicles. *Atmos. Meas. Tech.* **2019**, *12* (6), 3123–3135. https://doi.org/10.5194/amt-12-3123-2019.

(184) Koppmann, R.; Wildt, J. Oxygenated Volatile Organic Compounds. In *Volatile Organic Compounds in the Atmosphere*; Blackwell Publishing Ltd, 2007; pp 129–172. https://doi.org/10.1002/9780470988657.ch4.

(185) Reimann, S.; Lewis, A. C. Anthropogenic VOCs. In *Volatile Organic Compounds in the Atmosphere*; Blackwell Publishing Ltd, 2007; pp 33–81. https://doi.org/10.1002/9780470988657.ch2.

(186) Bari, M. A.; Kindzierski, W. B.; Wheeler, A. J.; Héroux, M. È.; Wallace, L. A. Source Apportionment of Indoor and Outdoor Volatile Organic Compounds at Homes in Edmonton, Canada. *Build. Environ.* **2015**, *90*, 114–124. https://doi.org/10.1016/j.buildenv.2015.03.023.

(187) CDC - NIOSH Pocket Guide to Chemical Hazards - Ethyl acetate https://www.cdc.gov/niosh/npg/npgd0260.html (accessed Oct 23, 2021).

(188) CDC - NIOSH Pocket Guide to Chemical Hazards - Cyclohexane

https://www.cdc.gov/niosh/npg/npgd0163.html (accessed Oct 23, 2021).

(189) Wong, G. K. S.; Webster, R. D. Active and Passive Adsorption of 47 Trace Atmospheric Volatile Organic Compounds onto Carbon Nanotubes. *RSC Adv.* **2021**, *11* (48), 29913–29919. https://doi.org/10.1039/d1ra05585b.

(190) Vallecillos, L.; Borrull, A.; Marcé, R. M.; Borrull, F. Presence of Emerging Organic Contaminants and Solvents in Schools Using Passive Sampling. *Sci. Total Environ.* **2021**, *764*, 142903. https://doi.org/10.1016/j.scitotenv.2020.142903.

(191) Salthammer, T. Very Volatile Organic Compounds: An Understudied Class of Indoor Air Pollutants. *Indoor Air* **2016**, *26* (1), 25–38. https://doi.org/10.1111/ina.12173.

(192) CDC - NIOSH Pocket Guide to Chemical Hazards - Acetaldehyde https://www.cdc.gov/niosh/npg/npgd0001.html (accessed Oct 24, 2021).

(193) CDC - NIOSH Pocket Guide to Chemical Hazards - n-Pentane https://www.cdc.gov/niosh/npg/npgd0486.html (accessed Oct 24, 2021).

(194) Alves, C. A.; Evtyugina, M.; Cerqueira, M.; Nunes, T.; Duarte, M.; Vicente, E. Volatile Organic Compounds Emitted by the Stacks of Restaurants. *Air Qual. Atmos. Heal.* **2015**, *8* (4), 401–412. https://doi.org/10.1007/s11869-014-0310-7.

(195) Mihucz, V. G.; Záray, G. Indoor Air Pollution. *Compr. Anal. Chem.* **2016**, *73*, 45–71. https://doi.org/10.1016/bs.coac.2016.02.003.

(196) Davis, M. E.; Blicharz, A. P.; Hart, J. E.; Laden, F.; Garshick, E.; Smith, T. J. Occupational Exposure to Volatile Organic Compounds and Aldehydes in the U.S. Trucking Industry. *Environ. Sci. Technol.* **2007**, *41* (20), 7152–7158. https://doi.org/10.1021/es071041z.

(197) Castorina, R.; Tysman, M.; Bradman, A.; Hoover, S.; Iyer, S.; Russell, M.; Sultana, D.; Maddalena, R. Volatile Organic Compound Emissions from Markers Used in Preschools, Schools, and Homes. *Int. J. Environ. Anal. Chem.* **2016**, *96* (13), 1247–1263. https://doi.org/10.1080/03067319.2016.1250892.

(198) Esteve-Turrillas, F. A.; Pastor, A. *Passive Air Sampling*; Elsevier Ltd, 2016; Vol. 73.

https://doi.org/10.1016/bs.coac.2016.04.003.

(199) Tuduri, L.; Millet, M.; Briand, O.; Montury, M. Passive Air Sampling of Semi-Volatile Organic Compounds. *TrAC - Trends in Analytical Chemistry*. Elsevier Ltd 2012, pp 38–49. https://doi.org/10.1016/j.trac.2011.08.007.

(200) Kot-Wasik, A.; Zabiegała, B.; Urbanowicz, M.; Dominiak, E.; Wasik, A.; Namieśnik, J. Advances in Passive Sampling in Environmental Studies. *Analytica Chimica Acta*. 2007, pp 141–163. https://doi.org/10.1016/j.aca.2007.09.013.

(201) Salim, F.; Górecki, T. Theory and Modelling Approaches to Passive Sampling. *Environ. Sci. Process. Impacts* **2019**, *21* (10), 1618–1641. https://doi.org/10.1039/c9em00215d.

Appendix

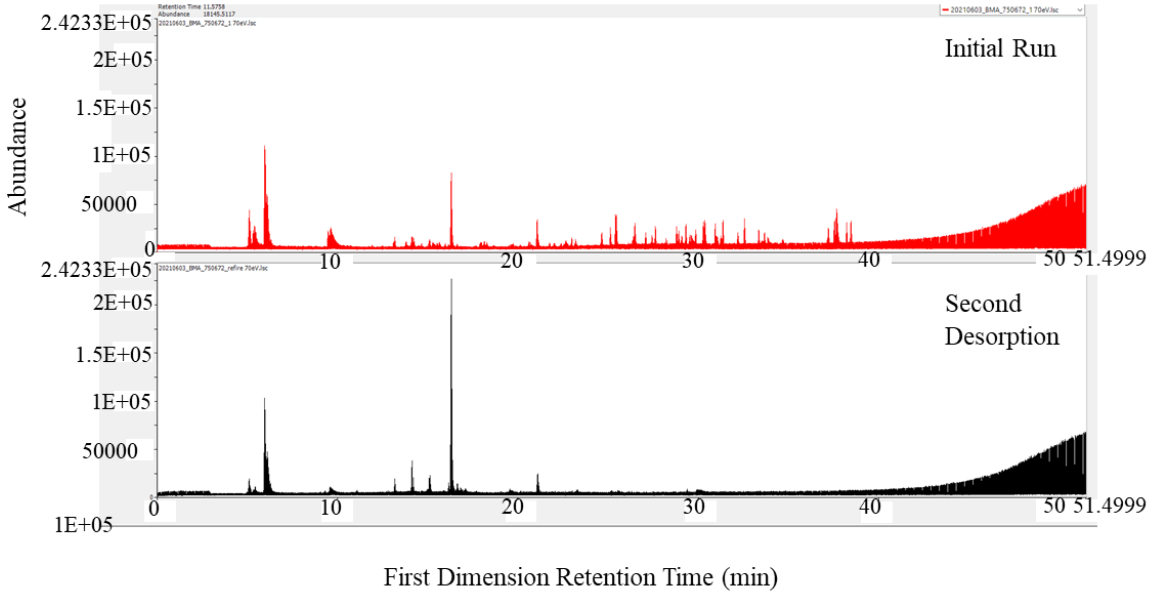


Figure A1: Chromatogram of Sorbent Tube Desorption Optimization with 0.24 ng Standard with 5-minute Desorption

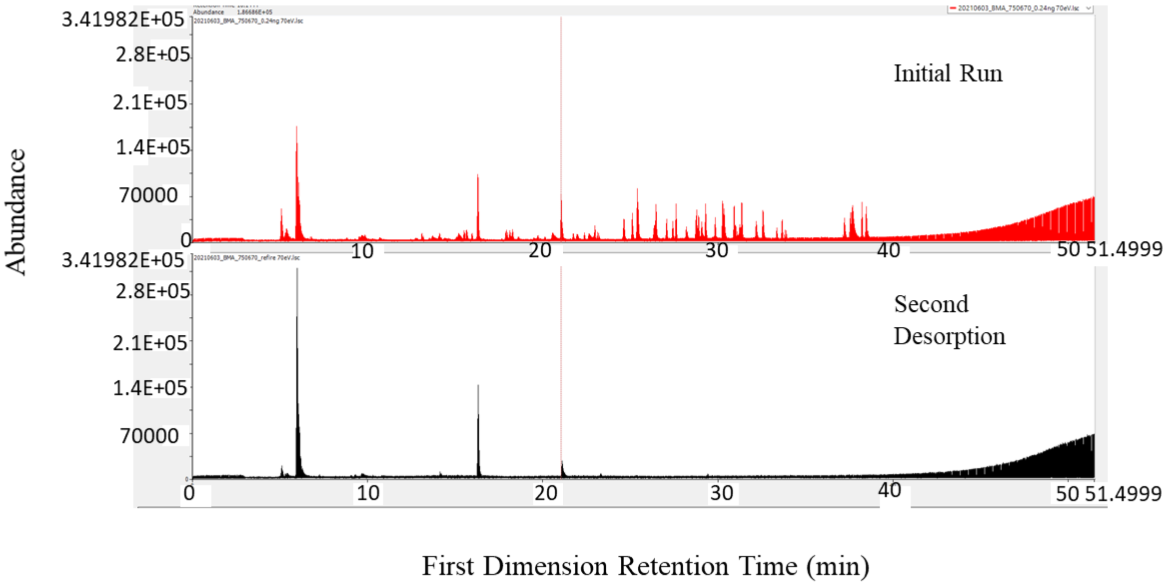


Figure A2: Chromatogram Showing Sorbent Tube Desorption Optimization with 0.24 ng Standard with 8-minute Desorption

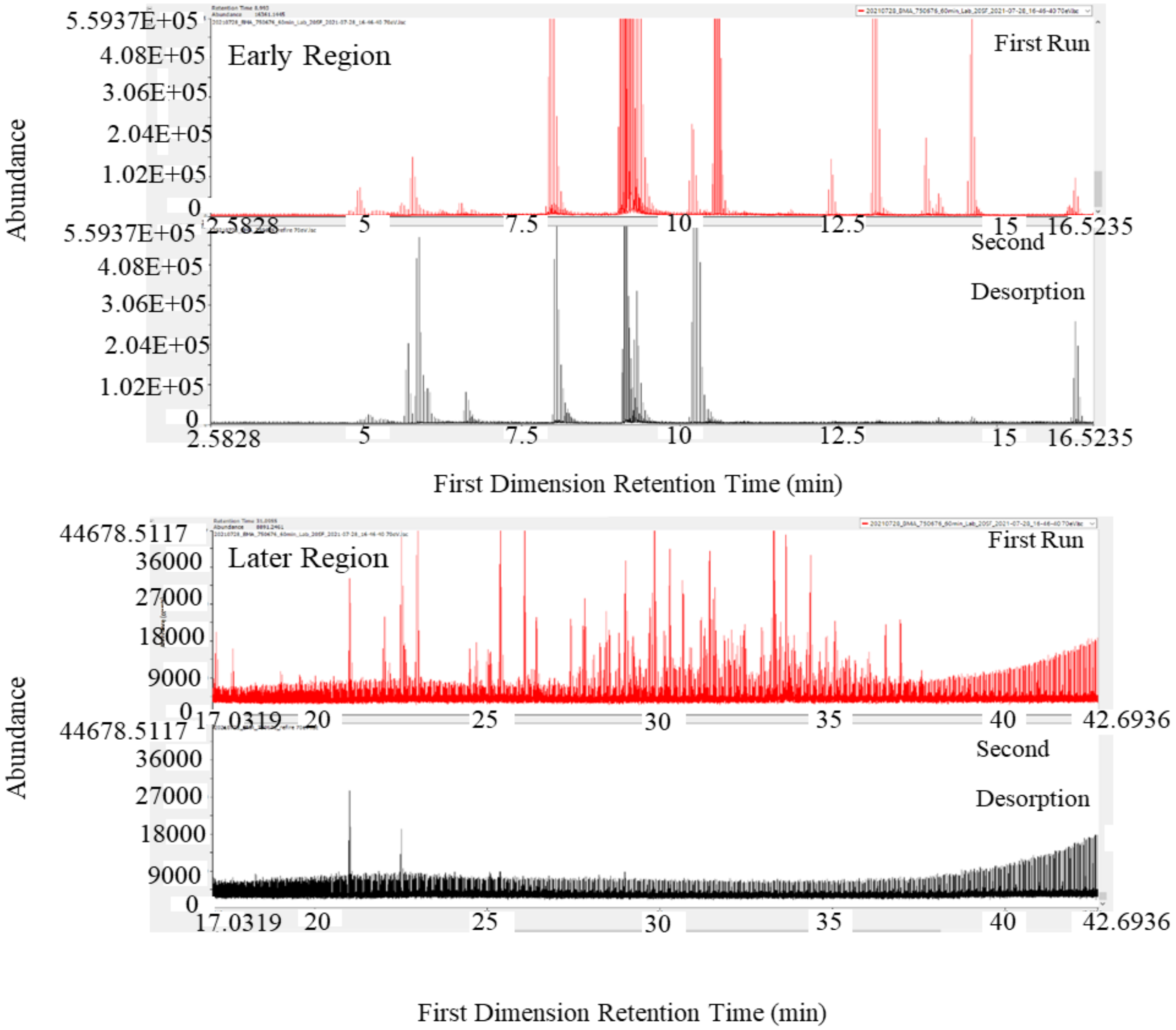


Figure A3: Real Sample Chromatogram Comparing Initial Desorption to Second Desorption in Early (Top) and Later (Bottom) Regions

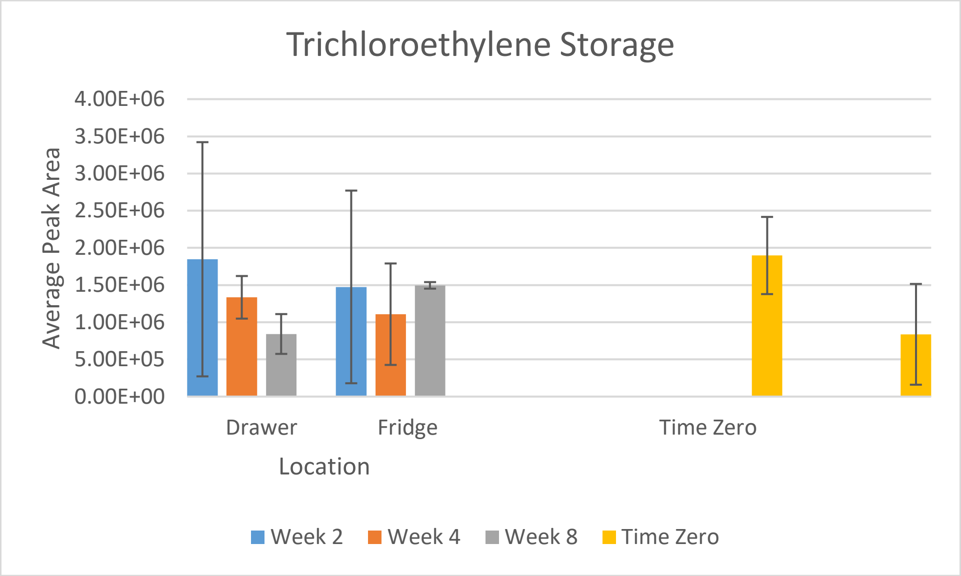


Figure A4: Changes in the Response of Trichloroethylene Over Time in Room Temperature and Refrigerated Locations

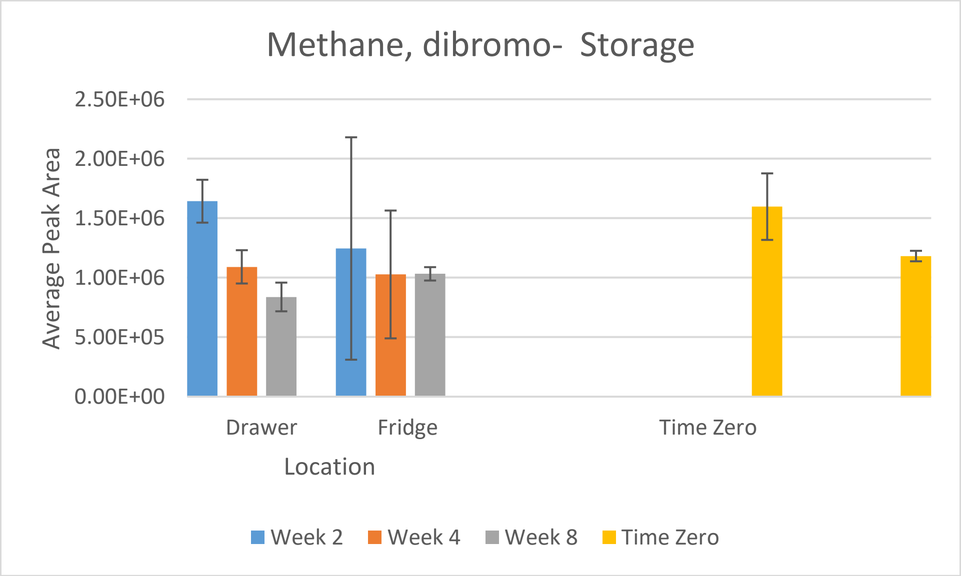


Figure A5: Changes in the Response of Dibromomethane Over Time in Room Temperature and Refrigerated Locations