MEASURING DIESEL EXHAUST GAS PHASE ORGANICS WITH A THERMAL DESORPTION PROTON TRANSFER REACTION MASS SPECTROMETER

By

MATTHEW HOWARD ERICKSON

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of MATTHEW HOWARD ERICKSON find it satisfactory and recommend that it be accepted.

____________________________________  
B. Thomas Jobson, Ph.D., Chair

____________________________________  
Tim VanReken, Ph.D.

____________________________________  
Shelley Pressley, Ph.D.

____________________________________  
Heping Liu, Ph.D.
ATTRIBUTION

Chapter 4 contains datasets provided by R. Subramanian from Droplet Measurement Technologies (soot), Chen Song at the Pacific Northwest National Laboratory (organic aerosol, particle counts), and Will Wallace at Washington State University (NO\textsubscript{X}, NO\textsubscript{2}). Chapter 5 VOC data collection and reduction from the LRRI exposure chambers was performed by Mylene Gueneron at Washington State University. Chapter 6 was written in collaboration with Chris Weaver at the United State Global Change Research Program.
MEASURING DIESEL EXHAUST GAS PHASE ORGANICS WITH A THERMAL DESORPTION PROTON TRANSFER REACTION MASS SPECTROMETER

Abstract
by Matthew Howard Erickson, Ph.D.
Washington State University
July 2013

Chair: B. Thomas Jobson

Photochemical processing of organic compounds from vehicle emissions forms ozone and increases organic particulate matter concentrations through the formation of secondary organic aerosol (SOA), which is a poorly understood, complex process in urban areas. Recent research has stressed the importance of intermediate volatility organic compounds (IVOCs) in vehicle emissions to SOA formation. A thermal desorption sampling technique was developed and coupled with a Proton Transfer Reaction Mass Spectrometer (PTR-MS) to measure C\textsubscript{10}-C\textsubscript{18} alkanes and other IVOC species. It utilizes an adsorbent resin to collect IVOCs and periodically desorb them into the PTR-MS for measurement. We demonstrated that the PTR-MS is sensitive to alkanes larger than C\textsubscript{9}, which fragment to a common set of ions following a C\textsubscript{n}H\textsubscript{2n+1} (n\geq3) pattern. The PTR-MS sensitivity to these alkanes was 1.5 Hz ppbv\textsuperscript{-1}, a factor of 6 lower than toluene, likely due to the proton affinities being less than water. The instrument was used in an urban field experiment and in the laboratory sampling diluted diesel and gasoline engine emissions. Relative to CO\textsubscript{2}, IVOC compound emissions of bicycloalkanes were a factor of 17 and naphthenic monoaromatics were a factor of 3 more abundant in diesel exhaust than in gasoline exhaust. The IVOC alkanes were a factor of 3.5 times more abundance in the diesel exhaust. We calculate the abundance of these IVOC compounds appears to be enough to
reconcile the measured to modeled discrepancy related to SOA formation reported from aerosol chamber experiments. The abundance of IVOC alkanes measured in the urban field experiment in Sacramento, CA reached nearly 3 ppbv and was approximately 40% lower on average than the total abundance of benzene and C₁-C₃ alkylbenzenes which are traditional SOA precursors. The IVOC alkanes were well correlated with soot concentrations (r²>0.95) during two large pollution events. This work indicates that IVOC compound emissions from diesel exhaust may have an important role in urban SOA chemistry.
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CHAPTER 1: INTRODUCTION

Vehicle emissions are a major source of primary air pollutants that impact human health (HEI, 2010). Photochemical processing of organic compounds from vehicle emissions also forms ozone and increases organic particulate matter concentrations through the formation of secondary organic aerosol (SOA) (Meng et al., 1997). While the photochemistry of ozone formation is reasonably well understood, the formation of secondary organic aerosol (SOA) in urban areas is a less understood, more complex process. Comparisons between measured and modeled organic aerosol concentrations in urban areas often reveal that models significantly underestimate organic aerosol concentrations (de Gouw et al., 2005; Volkamer et al., 2006; Kleinman et al., 2008). This discrepancy may arise from underestimation of SOA formation rates from organic compounds due to underestimating organic compound emission rates in models. Organic compounds are emitted from a wide variety of sources in urban areas. Vehicle emissions of aromatic compounds and biogenic emissions of monoterpenes are known to be important sources of SOA precursor compounds (Odum et al., 1996). While organic compound emissions from spark ignition (gasoline) vehicles are reasonably well known less is known about emissions from diesel engine vehicles. It has been suggested that diesel engine emission inventories for organic compounds are biased to the condensed phase by virtue of how emissions sampling is done (Robinson et al., 2007; Shrivastava et al., 2008). Components of organic particulate matter emitted from diesel exhaust likely partition back to the gas phase as the exhaust plume becomes diluted, creating a pool of compounds that act as precursors for SOA which would not be accounted for in emission inventories and chemical transport models (Robinson et al., 2007). These compounds have been labeled intermediate volatile organic
compounds (IVOCs) to distinguish them from more volatile organic compounds (VOCs) associated with spark ignition engine exhaust.

IVOCs are classified as organic compounds with a saturation vapor pressure between $1.33 \times 10^{-4}$ and $1.33 \times 10^{-1}$ hPa ($10^{-4}$ and $10^{-1}$ Torr) at 25 °C (Robinson et al., 2007; Presto et al., 2009). For the n-alkanes this vapor pressure range corresponds to dodecane ($C_{12}$) through to octadecane ($C_{18}$) and compounds within this vapor pressure range comprise approximately 46% of diesel fuel (Gentner et al., 2012) and about 8% of diesel exhaust (Schauer et al., 1999). Laboratory tests have shown significant formation of SOA from long chain n-alkanes, branched alkanes, and cyclic alkanes found in diesel engine exhaust (Lim and Ziemann, 2005; Jordan et al., 2008; Samy and Zielinska, 2009; Tkacik et al., 2012). Recasting a portion of the primary organic particulate matter emissions from diesel vehicle exhaust as reactive gas phase material indeed results in significantly more SOA and better agreement with measurements (Shrivastava et al., 2008; Dzepina et al., 2009; Murphy and Pandis, 2009; Hodzic et al., 2010; Pye and Seinfeld, 2010). However, the actual emission rates and photochemistry of these compounds is not well understood. The general importance of diesel engine emissions to urban air chemistry is gaining significance in the United States as gasoline engine roadway emissions of CO and VOCs are steadily decreasing (Parrish et al., 2009, Schneidemesser et al., 2010) while roadway diesel fuel use has been increasing at a faster rate compared to gasoline usage (Dallman and Harley, 2010). Recently Gentner et al. (2012) concluded that diesel engine vehicle emissions were more important than gasoline engine vehicle emissions as a source of SOA for urban regions in California. The opposite conclusion was drawn by Bahreini et al. (2012) for SOA formation in the Los Angeles, CA urban plume. There is a need to better quantify the abundance of organic
compounds associated with diesel engine exhausts to clearly understand their role on urban air photochemistry and health.

1.1. Model and Emission Inventories to Observation

Observations of urban aerosols have reported the presence of more secondary organic aerosol than primary organic aerosols, while model results (Vutukuru et al., 2006; Pun et al., 2003) and estimations (Turpin and Huntzicker, 1995; Cabada et al., 2004) point to primary organic aerosol (POA) being the dominant urban organic aerosol. This discrepancy lies with how the models and emission inventories deal with POA. In models POA is treated as being nonvolatile, but this has been shown to be inaccurate through experimentation and modeling (Shrivastava et al., 2006). POA emission rates from vehicles are determined by sampling exhaust at high particulate matter concentrations and IVOC compound mass partitions to the particulate phase (Shrivastava et al., 2006; Lipsky and Robinson, 2006). Utilizing a formula to calculate the partitioning coefficient (ratio of gas phase concentration to the particle phase concentration), IVOCs are volatile enough that they will exist primarily in the gas phase for a typical urban PM mass concentration (Liang, et al., 1997). For example, the partitioning coefficient for dodecane and octadecane are 2.84x10^{-8} and 3.77x10^{-5} at 30 °C. Under an atmospherically relevant particle loading of 10 µg m^{-3}, the gas to aerosol ratio of dodecane and octadecane are 3.527x10^{6} for dodecane and 2.65x10^{3} for octadecane at 30 °C. This means there is roughly 1000 to 1,000,000 times more mass found in the gas phase than aerosol phase. Depending on the volatility of the species, as an exhaust plume becomes diluted the IVOCs will partition to the gas phase. This leads to additional SOA precursor material that may not be accounted for in emission inventories and model chemistry. In general these large organic compounds are difficult to measure which results in IVOCs being generally uncharacterized in
emission inventory work and in urban air monitoring. Overall, models and emission inventories not only leave these IVOCs unquantified, but they do not account for the resulting SOA formation. Robinson et al., (2007) observed SOA formation through chamber experiments by photochemical aging of diluted diesel exhaust with ultraviolet light. Calculations of the SOA yields from traditional SOA precursors for these experiments suggested that the traditional SOA precursors contributed to less than 15% of the SOA. They suggest that the remainder of the SOA is a result of IVOC species oxidation. It becomes apparent the characterization of IVOC species is crucial for understanding SOA formation in urban environments.

1.2. Urban IVOC Alkane Measurements

Little appears to be known about the overall abundance of IVOC species in urban environments. Due to their low concentration, low volatility, and the very large number of compounds that comprise diesel exhaust, it is difficult to speciate and quantify these species using gas chromatography sampling and analysis methods. Zielinska et al. (1996), Lai et al. (2004), Lough et al. (2005), and Hung-Lung et al. (2007) reported a relatively wide range of VOCs and IVOC compounds and are useful to assess their relative abundances. Lai et al., (2004) measured n-alkanes up to pentadecane in Kaohsiung, Taiwan. Average concentrations of individual C_8 to C_{15} n-alkane compounds ranged from 0.37 to 2.72 µg m^{-3} with the total sum of these alkanes as high as 16.14 µg m^{-3}. The ratio of n-alkanes to toluene was 0.30 for the Taiwan study, suggesting a potentially significant contribution of diesel exhaust organic gases to the organic burden in polluted urban air. A tunnel study performed by Zielinska et al., (1996) reported concentrations of individual C_{10} to C_{15} n-alkanes reaching nearly 4 ppbv. The tunnel had 2 bores. In the bore dominated by diesel engine vehicle traffic (68% of vehicles) the n-alkane to toluene ratio was 0.61, while in the bore dominated by spark ignition engine traffic
(98% of vehicles) the n-alkane to toluene ratio was ~0.1. Lough et al. (2005) measured the emission rates (mg L\(^{-1}\) fuel) of n-alkanes up to dodecane and isoalkanes up to C\(_{12}\) during roadway tunnel measurements in Milwaukee, WI. The highest alkane emissions were observed in the Howell tunnel during the winter. The resulting C\(_{8}\) to C\(_{12}\) n-alkane and isoalkane emissions totaled 231 mg L\(^{-1}\). Comparing this to the observed toluene emission rate of 594 mg L\(^{-1}\) resulted in an alkane to toluene ratio of 0.39. Hung-Lung et al. (2007) sampled from a tunnel in southern Taiwan. They sampled from outside, at the entrance, and in the center of the tunnel. They reported concentrations of C\(_{4}\) to C\(_{11}\) n-alkanes from two different sampling periods. The concentration of C\(_{8}\) to C\(_{11}\) n-alkanes at the center of the tunnel totaled 6.9 and 22.1 µg m\(^{-3}\) during the first and second sampling periods respectively. Comparing this to the observed toluene concentrations of 15 and 25 µg m\(^{-3}\) during the first and second sampling periods respectively results in alkane to toluene ratios of 0.46 and 0.88 respectively. Given the differences in range of alkanes reported, the alkane to toluene ratios ranged from 0.1 to 0.88 with most of the ratios at ~0.4. These chromatography based methods are limited to volatile compound analysis because of limitations of air sampling methods such as sampling into canisters, and by typical chromatographic methods that are focused on resolving complex mixtures of low boiling point compounds that constitute gasoline exhaust compounds at the expense of resolving high boiling point IVOC compounds (> C\(_{12}\)) associated with diesel exhaust. While n-alkanes are among the most abundant individual components of diesel exhaust they likely represent only a portion of the overall mass emissions of saturated and aromatic compounds. The lack of a good analytical method to measured IVOC compounds in the gas phase and their potential importance as SOA precursors in urban areas motivates this research to develop a unique analytical method to
measure IVOC compounds using a thermal desorption sampler coupled to a proton transfer reaction mass spectrometer (PTR-MS).

Thermal desorption sampling and analysis using a PTR-MS has been applied to some areas of analysis (Holzinger et al., 2010; Crespo et al., 2012) but to our knowledge has not been applied to measure IVOC species in urban air. Holzinger et al. (2010) utilized the thermal desorption sampling to measure the chemical composition of organic aerosol. The instrument was utilized during a series of smog chamber experiments and during the EUCAARI-IOP campaign at the Cabauw Experimental Site for Atmospheric Research (CESAR) site located in the Netherlands in May 2008. Crespo et al. (2012) tested the fidelity of coupling off-line thermal desorption with the PTR-MS through a series of laboratory experiments. This entailed collecting ethanol, acetaldehyde, acetone, isoprene, benzene, toluene, xylene, and alpha-pinene onto a mixture of sorbents (Carbograph TD and Carbopack X) and testing the linearity of the storage capacity, reproducibility, and storage capacity over time.

1.3. Thermal Desorption Sampling of IVOCs

Due to their low concentration, low volatility, and the very large number of compounds that comprise diesel exhaust, it is difficult to speciate and quantify these species in urban air by gas chromatography methods (Zielinska et al., 1996). While n-alkanes are among the most abundant individual components of diesel fuel (Gentner et al., 2012; Vendeuvre et al., 2005; Isaacman et al, 2012) and exhaust (Schauer et al., 1999), branched alkanes, cycloalkanes, and monoaromatic compounds are also very abundant and would be expected to be present in urban air, though rarely reported (Lewis et al., 2000). The method developed for this dissertation was to use a thermal desorption sampler to preconcentrate IVOC compounds from an air sample then analyze using a PTR-MS. The sampling approach was to alternate traditional VOC sampling by
the PTR-MS with analysis of heavier organics collected on an adsorbent resin and periodically thermally desorbed into the PTR-MS. In this way the abundance of IVOC compounds can be compared to the abundance of VOC compounds using the same principle of measurement. The PTR-MS identifies organics by molecular weight (MW) hence isomers are lumped together, simplifying the analysis of complex mixtures and improving detection of larger organic compounds with many isomeric forms.

Gasoline and diesel engine emissions are dominated by many of the same VOC compounds such as light alkenes, alkanes, and monoaromatics (Schauer et al., 1999., Schauer et al. 2002) so distinguishing between diesel engine and gasoline engine emissions using IVOC compound fingerprints became a goal as the project developed. Many compounds undergo dissociative proton transfer reactions in the PTR-MS producing a host of fragment ions. A significant part of the development of the IVOC sampler was understanding fragmentation patterns of both VOC and IVOC compounds found in urban air to better understand potential interferences and approaches to reducing positive interferences from much more abundant VOC compounds.

1.4. IVOC Sampler Deployment

The IVOC sampler was deployed to Sacramento, CA during the Carbonaceous Aerosol and Radiative Effects Study (CARES) from June 2nd to the 28th in 2010. CARES was funded by the Department of Energy Atmospheric Sciences Research (ASR) program with the objective of investigating the evolution of optical and physiochemical properties of urban aerosols as they are transported from an urban area to a forested area (Zaveri et al., 2012). It involved 27 different institutions at two different sites. The first site (T0) was located at American River College in Sacramento, CA and the second downwind site (T1) was located at Northside School in Cool,
CA. Instrumentation was deployed at both sites to monitor meteorology, solar radiation flux, trace gas concentrations and the particle size, concentration, composition, and optical properties. The objectives of the campaign as described by Zaveri et al. (2012) were to determine:

“1) how do anthropogenic and biogenic precursors interact to form SOA, 2) how rapidly does black carbon mix with other species, and what are the relative contributions of condensation and coagulation to black carbon mixing state evolution, and 3) what are the effects of aerosol mixing state and organic (primary and secondary) species on the associated optical and cloud condensation nuclei activation properties?”

The PTR-MS and IVOC sampler were deployed at the T0 site and housed inside WSU’s Mobile Atmospheric Chemistry Lab (MACL). This provided an opportunity to test the IVOC sampler in an urban setting to measure IVOC abundance and was related to objective #1 of the CARES study.

In the spring of 2012, the IVOC sampler was also used to characterize engine emissions at the Lovelace Respiratory Research Institute (LRRI) exposure lab as part of University of Washington’s (UW) EPA funded Center for Clean Air Research (CCAR). The purpose of the CCAR is to better understand cardiovascular health effects of roadway emissions through field measurements to document exposure and through lab studies of animal and human subject testing. Diesel engine exhaust causes cardiopulmonary and immune responses in animal models (McDonald et al., 2011). The experiments at LRRI involved sampling diesel and gasoline engine exhausts from inhalation exposure chambers. Sampling was performed with colleagues from the University of Washington who deployed their field measurement equipment along with Washington State University Laboratory for Atmospheric Research’s PTR-MS and Aerosol Mass Spectrometer. The emissions from the engines and facility description are described in
more detail in McDonald et al. (2004; 2007; 2011). The motivation behind the LRRI research was the observation of increased toxicity from mixtures of diesel and gasoline exhausts beyond what is expected from a combination of the effects of pure exhausts. We hypothesized that this increased effect may be due to heavier gasoline compounds condensing onto particles present in the diesel exhaust. The vapor pressures of gasoline emissions are generally high enough that they will be found in gas phase in typical urban environments. However, under high particle loads such as used in animal exposure studies at LRRI, the larger, less volatile species of gasoline exhaust will partition onto the diesel engine particles enhancing their toxicity. The facility can blend diesel and gasoline engine exhaust in different proportions. Over a series of tests, the engine load was varied and the exhaust diluted to different extents with clean, dry air. This provided an excellent opportunity to characterize vehicle exhaust composition with the IVOC sampler and potentially examine gas-particle partitioning of IVOC compounds.

1.5. Dissertation Overview

This dissertation is presented in four research oriented chapters with an additional chapter presenting policy work that resulted from an Atmospheric Policy Trajectory (APT) internship with the United States Global Change Research Program in Washington, DC from July 25th to October 25th, 2012. Chapter 2 presents the experimental methods and techniques. It provides an overview of the theory of operation of the proton transfer reaction mass spectrometer to illustrate how its operation was modified in this research to allow for measurement of IVOC compounds by thermal desorption. The governing reactions and physics of the PTR-MS principle of measurement are described and how they affect the interpretation of data. The chapter also describes in detail the development and operation of the IVOC Sampler, including the construction and automation of the sampler and performance characterization including tests.
done in the lab and in the field. The chapter covers interpretation and processing of the data, how the system is calibrated, and method detection limits. Chapter 3 is an experimental methods manuscript submitted in June 2013 to the journal Atmospheric Measurement and Techniques. The introductory material from this manuscript has been removed and is included in this introductory chapter. The manuscript presents the thermal desorption PTR-MS technique for measuring IVOC compounds. Sections that were included in the manuscript were removed when the information was explained in Chapter 2. Chapter 4 presents a manuscript detailing the deployment of the PTR-MS and IVOC sampler during the CARES field experiment. The manuscript is being prepared for submission to a CARES special issue in the journal of Atmospheric Chemistry and Physics. The chapter is formatted in journal manuscript form. It describes results of the PTR-MS based VOC measurements, abundance of IVOC alkanes as measured by thermal desorption PTR-MS which constitute a new result, and assessment of the IVOC alkane data through correlations with vehicle emissions including soot. The measurement of total IVOC alkanes in urban air constitutes a new observation and an important first assessment of their abundance in urban air. Chapter 5 presents a manuscript detailing the deployment of the PTR-MS and IVOC sampler during engine exhaust chamber monitoring at LRRI. This manuscript is being prepared for submission after consultation and input from collaborating authors at LRRI and UW. A brief overview of the laboratory setup and instrumentation is presented, along with details about the IVOC sampler method. It discusses the composition of gasoline and diesel exhaust as observed by the IVOC sampler and dehumidified PTR-MS sampling, and documents the role of engine load on relative abundances. It presents a vehicle exhaust signature mechanism that may help quantify relative contributions of diesel and gasoline within a mixture, looks at relative abundances of IVOC species to CO2 to estimate
potential emission rates and, estimates the SOA yields of IVOC species to assess their impact on urban air quality. Chapter 6 presents a policy paper resulting from the APT internship experience. The chapter describes the need and process for establishing a greenhouse gas information system (GHGIS) for the Unites States, including the need for a centralized GHGIS, how it should be structured, and assesses some of our current capabilities. After identifying important knowledge gaps concerning GHG observations, modeling, and communication, an outline for bringing together an integrated GHGIS is proposed along with what immediate steps could be taken to achieve its implementation.
1.6. References


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CHAPTER 2: EXPERIMENTAL

2.1. PTR-MS Operation

The proton transfer reaction mass spectrometer (PTR-MS) is a real-time volatile organic compound (VOC) analyzer sold by Ionicon Analytik (Austria). Due to its fast response, low detection limits, and wide range of observable species, the PTR-MS has been applied to a large variety of applications from observing bed bug emissions (Kilpinen et al., 2012) to measuring emissions from decaying food (Phan et al., 2012). What the PTR-MS can observe depends upon the proton affinity (PA) of the species. Figure 2.1 displays proton affinities for compounds typically found in urban air. Any species with a PA less than water will not be observed. While the PTR-MS can observe a wide range of species, it is blind to the more abundant trace gases in air (CO, CO$_2$, NO$_x$, O$_3$, SO$_2$, CH$_4$, etc.).

The components of the PTR-MS can be broken down into four main systems, the ion source, the sample inlet, the drift tube, and the mass spectrometer and detector. The ion source generates the reagent ion (H$_3$O$^+$) that drives the proton transfer reactions. The sample inlet allows for ambient sampling at different flows while maintaining constant pressure in the drift tube. The drift tube is where the proton transfer reactions occur, creating organic ions for detection. The mass spectrometer selects what ions to measure and transports them to the detector where the response is measured. This chapter will describe the different components of the PTR-MS, discuss the proton transfer reactions, and detail the interpretation of data, sensitivities, measurement error, and detection limits.
2.1.1. Principle of Operation

The governing reaction of the PTR-MS is the proton transfer from the reagent ion H$_3$O$^+$ to an organic species R to form an organic ion RH$^+$ and water:

$$\text{H}_3\text{O}^+ + \text{R} \rightarrow \text{H}_2\text{O} + \text{RH}^+ \quad (R1)$$

The resulting ion equals the molecular weight of the species plus one (M+1). This reaction is exothermic if the proton affinity (PA) of the organic R is larger than the PA of water (697 kJ mol$^{-1}$) and the reaction will occur at the collisional rate limit $k_c$ (cm$^3$ molecule$^{-1}$ sec$^{-1}$). The collision rate constant $k_c$ can be calculated from the polarizability and dipole moment of the organic R (Chesnavich et al., 1980; Su and Chesnavich, 1982) and is discussed in further detail below. The rate constant can be used to determine calibration factors for the PTR-MS.

For species that have a proton affinity slightly larger than water, a back reaction can occur that transfers the proton from the organic R back to the water molecule:

$$\text{RH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{R} \quad (R2)$$

This reaction is endothermic, but there is enough kinetic energy to drive this back reaction. For example, the PA of formaldehyde is 713 kJ mol$^{-1}$ and experiences a water vapor dependent back reaction, which complicates the interpretation of the data (Jobson and McCoskey, 2010). The sensitivity of formaldehyde and species with a similar PA are a function of water vapor concentration in the drift tube. The water vapor correction for a given species can be estimated through laboratory experiments by observing the changes in the sensitivity under varying humidity.
2.1.2. PTR-MS Components

2.1.2.1. Ion Source

The ion source consists of custom stainless steel rings from Ionicon. The basic parts consist of a cathode tube and an intermediate chamber. The ions are created through a hollow cathode discharge process where electrons are emitted and impact with water vapor to create $H^+$, $O^+$, $H_2O^+$ and $OH^+$ ions. The ions are transported to the intermediate chamber where they react with $H_2O$ to produce an intense source of $H_3O^+$. The water vapor flow is controlled by 0-10 standard cubic centimeters per minute (sccm) low pressure drop mass flow controller (MFC) connected to a stainless steel cylinder filled with deionized water run through a Millipore purifier. The MFC is designed to operate under low pressures and the vapor pressure of water within the cylinder is sufficient to drive the MFC. The PTR-MS software allows for control over the voltages applied to the source, which allows the user to essentially tune the instrument. The goal is to vary the voltages to increase $H_3O^+$, but keep the relative amounts of $O_2^+$ and $NO^+$ to a minimum. Typical operation calls for $O_2^+$ to be under 2% and $NO^+$ to be under 0.14%. These ions are typically formed from air back streaming into the source. However, if the user is unable to decrease the levels of $O_2^+$ and $NO^+$ through tuning, a leak check should be performed. The source is controlled by the source current, water vapor flow and the US and USO voltages displayed in Figure 2.2. The typical settings range from 5 to 7 mA source current, 8 sccm water vapor flow, 250 V on the US, and 80 V on the USO.

2.1.2.2. Sample Inlet

The main objective of the sample inlet is to sample at a constant flow and maintain a constant pressure within the drift tube. This is accomplished through the use of capillary tubes and a Bronkhorst electronic pressure/meter controller (P-702C-FAC-22-V). A fraction of the
sample is pulled through a 20 cm, 0.02” inner diameter (ID) capillary tube. The capillary tube typically decreases the pressure to 555 to 610 mbar, which is regulated by the Bronkhorst pressure controller. A portion of this sample is pulled through a second capillary tube (40 cm, 0.01” ID), which decreases the pressure to ~2mbar, and into the drift tube. A schematic of the sample inlet is displayed in Figure 2.3. The sample flow through the inlet valve is controlled by a needle valve and typically ranges from 100 to 300 sccm.

2.1.2.3. Drift Tube

The ion source and sample inlet are both connected to the drift tube, which is where organics undergo the proton transfer reaction with the reagent ion (H_3O^+). The use of a drift tube allows for control over the conditions that effect the proton transfer reaction. The pressure, temperature, and value of the electric field impact the chemistry. An electric field is applied to the drift tube, which determines the kinetic energy of the molecules and is the main component in transporting the ions to the mass spectrometer. The value of the electric field is often larger than 30 V cm\(^{-1}\). The design of the drift tube consists of 10 stainless steel rings (including the sample ring) that are separated by Teflon rings, which results in a drift tube length of 9.2 cm. A network of resistors connects the steel rings to create an electric field that drives ions along the drift tube. An example of the drift voltages can be observed in Figure 2.2 for a drift voltage setting of 324 V, which results in an electric field of ~35 V cm\(^{-1}\).

The velocity of ions through the drift tube (\(v_d\)) is a function of the ion mobility (\(\mu\)) and the electric field \(E\).

\[
v_d = \mu \times E
\]

(2.1)

The ion mobility is a function of pressure and temperature, or the number density (N) of the gas in the drift tube.
\[ \mu = \mu_0 N_0 N^{-1} \]  

(2.2)

where \( \mu_0 \) is the reduced ion mobility at standard pressure and temperature conditions (\( N_0 \)).

Substituting equation 2.2 into equation 2.1, the drift velocity can be defined as a function of the reduced ion mobility, the number density (\( N_0 \)) of gas at standard temperature and pressure (273 K, 1 atm), the number density of gas in the drift tube (\( N \)), and the electric field (\( E \)).

\[ v_d = \mu_0 N_0 X E / N \]  

(2.3)

The ion drift velocity is determined by the ratio of the electric field over the number density of gas in the drift tube. The ratio of \( E/N \) is referred to as the Townsend number (Td) with 1 Td = \( 10^{-17} \) V cm\(^2\). The Townsend number characterizes the PTR-MS drift condition and is typically operated in the range from 80 to 150 Td. The reaction time within the drift tube can be determined by dividing the drift tube length (9.2 cm) by the drift velocity. For example, at a drift temperature of 70 °C, drift pressure of 2.1 mbar, and drift voltage of 325 V, the ion drift velocity would be 59,092 cm/s, which results in a reaction time of 156 \( \mu \)sec.

For this research the PTR-MS was typically run at two conditions for ambient measurements: 80 Td and 120 Td. The 120 Td condition was the standard for sampling when no sample pre-conditioning (dehumidifier or IVOC sampler) was performed. The drift tube settings typically range from a drift pressure between 2.0 and 2.2 mbar, a drift voltage between 300 and 600 V, and a drift temperature between 30 and 70 °C. There are a number of advantages of operating at 80 Td. At lower Td operation the drift velocity is lower thus increasing the reaction time and increasing instrument sensitivity. Lower ion velocity also reduces the likelihood of dissociative proton transfer reactions. Reduced fragmentation aids in the interpretation of the PTR-MS mass spectrum. The drawback is this also results in increased ion clustering with water vapor. This clustering is a function of air sample humidity, so reducing humidity will limit this
effect. To counter humidity, the VOC inlet is outfitted with a dehumidifier to remove water vapor and the IVOC inlet utilizes dry N\textsubscript{2} as the desorption carrier gas. Both methods effectively remove water vapor and allow for 80 Td operation. If the PTR-MS is outfitted with the dehumidifier or IVOC system, the conditions are typically set to 80 Td. The typical 80 Td setting are a drift pressure of 2.1 mbar, drift voltage of 325 V, and a drift temperature of 70 °C. The high drift temperature is crucial when using the IVOC system to reduce any wall losses of low vapor pressure species.

2.1.2.4. Quadrupole Mass Spectrometer and Electron Multiplier

For ion selection, the PTR-MS utilized a QMS 422 quadrupole mass spectrometer (QMS). The QMS installed in the PTR-MS was from Pfeiffer Vacuum and consisted of four parallel metal rods. A direct current (DC) voltage superimposed over a radio frequency (RF) voltage field was applied to each pair of rods. Ion selection was achieved by varying the voltages. This caused unstable trajectories in ions that were lighter (through DC) and heavier (through RF) than the selected mass to charge ratio (\(m/z\)) value and they collided with the rods.

The PTR-MS was installed with a Model AF 140 secondary electron multiplier (SEM) from ETP Electron Multipliers. The purpose of the SEM is to multiply the signal through inducing secondary electron emission from the \(m/z\) ions selected from the QMS. When an electron collides with a secondary emissive material (ETP material is proprietary) it induces the emission of 1 to 3 more electrons. This process can be repeated many times (typically 12 to 24) by applying electrical potentials between the plates leading to a large multiplication of electrons and therefore a magnification of the signal. This is critical as only a small percentage of ions are actually measured with the SEM.
2.1.3. PTR-MS Characteristics

2.1.3.1. PTR-MS Mass Spectrum

PTR-MS operation allows for customizable measurement procedures. A user can operate the PTR-MS in bar scan mode or multiple ion detection (MID) mode. Bar scan mode measures each \( m/z \) ion over a defined range or ranges. The dwell time and resolution can be specified for a particular range. The dwell time is the time spent measuring the ion and the resolution is the \( m/z \) range the QMS allows to pass for a particular setting. The MID mode allows for the measurement of a selection of ions. The user defines which \( m/z \) ions will be observed and can individually set the dwell time and resolution. An example bar scan spectra is shown in Figure 2.4. The spectrum includes responses in counts per second (Hz) from ambient species as well as multiple ions that are measured for diagnostics.

2.1.3.2. Diagnostic Ions

The typical diagnostic ions are \( m/z \) 21 \([\text{H}_3^{18}\text{O}^+]\), 30 \([\text{NO}^+]\), 32 \([\text{O}_2^+]\), 37 \([\text{H}_3\text{O}^+(\text{H}_2\text{O})]\), 39 \([\text{H}_3\text{O}^+(\text{H}_2^{18}\text{O}) \text{ or } \text{H}_3^{18}\text{O}^+(\text{H}_2\text{O})]\), and 55 \([\text{H}_3\text{O}^+(\text{H}_2\text{O})_2] \). The \( m/z \) 21 ion is measured to record \( \text{H}_3\text{O}^+ \) instead of \( m/z \) 19. Observing the \( \text{H}_3\text{O}^+ \) signal at \( m/z \) 21 and correcting for the isotopic abundance of \( ^{18}\text{O} \) allows for measurement of \( \text{H}_3\text{O}^+ \) ions with 1/490 of the signal. This is done to reduce subjecting the detector to high count rates. Standard tuning of the PTR-MS entails reaching millions of counts per second (MHz) of \( \text{H}_3\text{O}^+ \). The \( \text{H}_3\text{O}^+ \) counts in Figure 2.4 are \( \sim 6 \times 10^6 \) Hz or 6 MHz. These high counts can help improve detection limits, reduce error, and increase sensitivity. The detector has a non-linear response at high count rates, so the high response at \( m/z \) 19 would be an issue. This effect is easily avoided by measuring the \( \text{H}_3\text{O}^+ \) isotope at \( m/z \) 21 and correcting for the isotopic abundance.
The m/z 30 and 32 ions refer to NO\(^+\) and O\(_2\)^+ respectively. Both of these ions will react with many VOCs in dissociative charge transfer reactions creating a wide range of fragment ions that muddles the interpretation of the PTR-MS mass spectrum as an M+1 mass spectrum. Therefore, it is important to limit the amount of NO\(^+\) and O\(_2\)^+ in the drift tube. Standard tuning of the PTR-MS entails keeping the amount of NO\(^+\) and O\(_2\)^+ to under 0.15% and 2% of the H\(_3\)O\(^+\) signal respectively. This reduces the interferences created from reactions with these ions to a negligible amount. In Figure 2.4, the NO\(^+\) and O\(_2\)^+ are 0.16% and 1.21% of the H\(_3\)O\(^+\) signal respectively.

The m/z 37, 39, and 55 ions measure the amount of water clusters. In addition to the proton transfer reaction, H\(_3\)O\(^+\) can cluster with H\(_2\)O:

\[
\text{H}_3\text{O}^+ + n\text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_n
\]

This reaction is highly dependent upon the humidity of the sample and drift tube conditions and creates interferences at m/z 37 and 55. The clustering can be reduced by increasing the kinetic energy (raising Td) in the drift tube; this is the essential purpose of the drift tube – to reduce water vapor clustering to cations. The H\(_3\)O\(^+\)(H\(_2\)O) water cluster produces a response at m/z 37. In Figure 2.4, the m/z 37 shows a high signal at 27% of the magnitude of H\(_3\)O\(^+\). To reduce subjecting the detector to high count rates, the \(^{18}\text{O}\) isotope of the water cluster is measured at m/z 39. This results in a factor of 250 less signal compared to m/z 37. The second water cluster H\(_3\)O\(^+\)(H\(_2\)O)\(_2\) observed at m/z 55 is not as abundant as the H\(_3\)O\(^+\)(H\(_2\)O) cluster. Observing these ions is important since the cluster ions can then undergo proton transfer reactions with organics with a high PA.

\[
\text{H}_3\text{O}^+(\text{H}_2\text{O}) + R \rightarrow \text{RH}^+ + 2\text{H}_2\text{O}
\]
This reaction is not often an issue, unless the concentration of H$_3$O$^+$(H$_2$O) is the same magnitude as H$_3$O$^+$. If this is the case, the organic will have to be normalized to both H$_3$O$^+$ and H$_3$O$^+$(H$_2$O) ions. Similar to this, organics can also form clusters:

$$RH^+ + nH_2O \rightarrow RH^+(H_2O)_n$$ \hspace{1cm} (R5)

The clustering complicates the interpretation of the mass spectrum, but is largely dependent upon the kinetic energy within the drift tube and the amount of water vapor in the sample air. Increasing the kinetic energy by increasing the Td or reducing water vapor in the sample air before it enters the drift tube are two methods that have been used to reduce clustering.

2.1.3.3. Mixing Ratio Calculation

The resulting signal from the proton reaction is observed as ion counts per second (Hz). The calculation of the mixing ratio [MR] of any given species [R] is a function of the H$_3$O$^+$ count rate [H$_3$O$^+$], the normalized sensitivity of the species [ncps$_{(R)}$] in units of Hz per ppbV per MHz H$_3$O$^+$, the observed count rate of the species [Sig$_{(R)}$], and the count rate of the background [BKG$_{(R)}$]. The relationship is expressed in the following formula:

$$MR = \frac{Sig_{(R)} - BKG_{(R)}}{ncps_{(R)} \times MHz H_3O^+}$$ \hspace{1cm} (2.4)

The magnitude of the signal has a linear relationship with the amount of H$_3$O$^+$ present in the drift tube. The more H$_3$O$^+$ present means more collisions, so typical tuning would result in achieving millions of H$_3$O$^+$ counts. Due to many factors that affect H$_3$O$^+$ counts, the signal is normalized by the MHz H$_3$O$^+$. This allows for comparison of data even if changes in H$_3$O$^+$ occurred.

The background signal is determined by measuring humid zero air or dry nitrogen blow off gas from a liquid N$_2$ dewar. Bar scan spectrums of dry nitrogen from a liquid dewer and zero air generated from lab air passed through a Pt catalyst (1% Pt on alumina spheres) are displayed in Figure 2.5. Both methods provide comparable background levels for most ions. The biggest
difference was observed in O\textsuperscript{2+} (m/z 32) with the dry nitrogen being 0.01\% and the catalyst zero air being 1.32\%. The relative signal to H\textsubscript{3}O\textsuperscript{+} for NO\textsuperscript{+} (m/z 30) and H\textsubscript{3}O\textsuperscript{+}(H\textsubscript{2}O) (m/z 37) were very similar, being on the order of 0.1\% and 1\% respectively for both.

2.1.3.4. Sensitivity Calculation

Sensitivity calculations for the PTR-MS were described by de Gouw and Warneke (2007). Instrument sensitivity can be derived from the equation of the concentration of H\textsubscript{3}O\textsuperscript{+} after reacting with organic R within the drift tube.

\[
[H_3O^+]_{\Delta t} = [H_3O^+]_0 \times e^{(-k[R]\Delta t)}
\]  
(2.5)

Where \([H_3O^+]_0\) and \([H_3O^+]_{\Delta t}\) are the concentrations of H\textsubscript{3}O\textsuperscript{+} at the beginning and end of the drift tube respectively. The proton-transfer rate coefficient is expressed as \(k\), the reaction time is \(\Delta t\), and \([R]\) is the concentration of organic R in the drift tube. In a similar manner, the concentration of H\textsubscript{3}O\textsuperscript{+} lost during the reaction can be expressed as:

\[
[H_3O^+]_{\text{lost}} = [H_3O^+]_0 - [H_3O^+]_{\Delta t}
\]  
(2.6)

Substituting equation 2.5 into equation 2.6 yields:

\[
[H_3O^+]_{\text{lost}} = [H_3O^+]_0 - [H_3O^+]_0 \times e^{(-k[R]\Delta t)}
\]  
(2.7)

Which can be simplified into:

\[
[H_3O^+]_{\text{lost}} = [H_3O^+]_0 \times (1 - e^{(-k[R]\Delta t)})
\]  
(2.8)

Assuming the only loss of H\textsubscript{3}O\textsuperscript{+} ions is through proton reactions with organic R, then \([H_3O^+]_{\text{lost}}\) would be equal to the concentration of RH\textsuperscript{+} generated.

\[
[RH^+] = [H_3O^+]_0 \times (1 - e^{(-k[R]\Delta t)})
\]  
(2.9)

As mentioned earlier, the instrument is tuned to have MHz H\textsubscript{3}O\textsuperscript{+}. If a negligible fraction of H\textsubscript{3}O\textsuperscript{+} ions reacts with organics in the drift tube -k[R]\Delta t will be very small. This can be achieved
by operating the drift tube at high $H_3O^+$ count rates. The generation of $RH^+$ can be expressed as the proton reaction of $H_3O^+$ with organic $R$ using the relationship $e^{-x} = 1-x$:

$$[RH^+] = [H_3O^+]k[R]\Delta t$$  \hspace{1cm} (2.10)

The reaction time $\Delta t$ in the drift tube can be expressed as a function of the length $L$ of the drift tube and the drift velocity $v_d$ of ions through the drift tube.

$$[RH^+] = [H_3O^+]k[R] \frac{L}{v_d}$$  \hspace{1cm} (2.11)

Substituting equation 2.3 from section 2.1.2.3 for drift velocity and solving for $[R]$ results in:

$$[RH^+] = [H_3O^+]k[R] \frac{N}{\mu_0 N_0 E}$$  \hspace{1cm} (2.12)

The concentration of organic $R$ can be expressed as a mixing ratio $R_{MR}$ by dividing by the number concentration $N$ in the drift tube:

$$R_{MR} = \frac{[R]}{N}$$  \hspace{1cm} (2.13)

Substituting this into equation 2.12 results in:

$$\frac{[RH^+]}{[H_3O^+]} = (R_{MR}N) \frac{kLN}{\mu_0 N_0 E}$$  \hspace{1cm} (2.14)

Assuming complete transmission of all ions from the drift tube to the detector, the ratio $[RH^+]$ and $[H_3O^+]$ can be expressed as the count rates observed for each in Hz $(Hz H_3O^+)^{-1}$.

$$\frac{Hz}{Hz H_3O^+} = R_{MR} \frac{kLN^2}{\mu_0 N_0 E}$$  \hspace{1cm} (2.15)

If it is assumed that there is a mixing ratio of 1 ppbv for organic $R$ and if the $H_3O^+$ signal is expressed as MHz, the equation can be transformed into a sensitivity:

$$\frac{Hz}{MHz H_3O^+ \times 10^6} = ppbv \times 10^{-9} \frac{kLN^2}{\mu_0 N_0 E}$$  \hspace{1cm} (2.16)

$$\frac{Hz}{MHz H_3O^+ \times ppbv} = 10^{-3} \frac{kLN^2}{\mu_0 N_0 E}$$  \hspace{1cm} (2.17)
The PTR-MS sensitivity is expressed as the ion signal observed at RH\(^+\) (Hz) per ppbv normalized by the \(\text{H}_3\text{O}^+\) signal (MHz \(\text{H}_3\text{O}^+\)). The units of sensitivity are expressed as Hz ppbv\(^{-1}\) (MHz \(\text{H}_3\text{O}^+\))\(^{-1}\) or ncps. However, equation 2.17 assumes complete transmission of both the RH\(^+\) and \(\text{H}_3\text{O}^+\) ions. In reality ion transmission through the mass spectrometer is a function of \(m/\varepsilon\). Therefore, a variable accounting for the relative ion transmission must be added to the equation.

\[
\text{ncps} = 10^{-3} \times \frac{kL}{\mu_0 N_0} \times \frac{N^2}{E} \times \frac{T_{RH^+}}{T_{H_3O^+}}
\]  

(2.18)

The sensitivity is a function of the reaction rate of proton-transfer \((k)\), the length of the drift tube \((L)\), the reduced ion mobility \((\mu_0)\), the number density \((N_0)\) of gas at standard temperature and pressure (273 K, 1 atm), the square of the number density of gas in the drift tube \((N)\), the electric field \((E)\), and the transmission efficiencies for RH\(^+\) and \(\text{H}_3\text{O}^+\) \((T_{RH^+}, T_{H_3O^+})\).

**Collisional Rates**

The reaction rate occurs at the collisional limit if the proton affinity of organic R is greater than H\(_2\)O (Bohme et al., 1979). The thermal rate is often described by the Langevin-Gioumousis-Stevenson equation (Chesnavich et al., 1980), which defines the thermal capture rate constant \(k_L\) as a function of the reduced mass \(\mu\) (amu), the polarizability \(\alpha\) (cm\(^3\)), and the electron charge \(q\) (esu).

\[
k_L = 2\pi q \left( \frac{\alpha}{\mu} \right)^{\frac{1}{2}}
\]  

(2.19)

This equation was determined to be a reasonable estimate of the upper bound of the rate constant; however, this work was further expanded upon by Su and Chesnavich (1982) to improve the accuracy. The equation for collisional rate \((K_{cap})\) was determined from an empirical fit to simulated computer runs performed by Chesnavich (1982).
The collisional rate is a function of polarizability ($\alpha$) and dipole moment ($\mu_D$) of the molecule, Boltzmann constant ($k_B$) and temperature ($T$) in Kelvin. The $K_{cap}$ is multiplied by $k_L$ to get an estimate of the drift tube rate constant. It is important to note that these equations calculate the thermal capture rate constants and do not account for the increased kinetic energies of ions in the drift tube. This introduces an unknown source of uncertainty when calculating theoretical reaction rate constants but is the best estimate that theory can provide.

Transmission Efficiencies

The transmission efficiencies are determined by sampling a particular organic at a high enough concentration to titrate away the $\text{H}_3\text{O}^+$ ions. The ratio of the $\text{RH}^+$ signal over the $\text{H}_3\text{O}^+$ signal is considered the relative transmission efficiency of the organic ion $\text{RH}^+$. Laboratory results have shown the transmission of varying organics relative to $\text{H}_3\text{O}^+$ to follow a curve as shown in Figure 2.6. Methanol ($m/z$ 33), acetonitrile ($m/z$ 42), acetone ($m/z$ 59), furan ($m/z$ 69), butanone ($m/z$ 73), benzene ($m/z$ 79), toluene ($m/z$ 93), p-xylene ($m/z$ 107), 1,2,4-trimethylbenzene ($m/z$ 121), trifluorobenzene ($m/z$ 133), diethylbenzene ($m/z$ 149), and trimethylbenzene ($m/z$ 163) were sampled in attempt to cover a wide molecular weight range. Fitting the data with a 3 order polynomial curve results in a transmission efficiency (TE) which can be expressed as a function of $m/z$ in the equation:

$$TE = -2.504 + 0.216 \times \left(\frac{m}{z}\right) - 0.00106 \times \left(\frac{m}{z}\right)^2$$  \hspace{1cm} (2.22)
This is an empirical representation of the transmission efficiency and does not assess what the individual causes are for the loss in transmission, but rather the overall effect. It can be noted that the transmission efficiency of most species is greater than that of H$_3$O$^+$. The transmission efficiency is normalized to the transmission at the peak of the curve, which occurs at m/z 105 with a transmission of 8.46. This results in a new transmission efficiency equation of:

$$TE = \frac{-2.504 + 0.216 \times \left(\frac{m}{T}\right) - 0.00106 \times \left(\frac{m}{T}\right)^2}{8.46}$$

(2.23)

Further investigation of the transmission efficiency is needed for the PTR-MS with an emphasis on characterizing the transmission of species with a MW larger than 140.

**Theoretical Sensitivities**

Combining equations 2.18 to 2.21, the sensitivity of an organic can be calculated. For example, toluene has a dipole moment of $0.343 \times 10^{18}$ esu cm, a polarizability of $12.9 \times 10^{-24}$ cm$^3$, and a reduced mass of 15.78 amu. Using equation 2.19 and an electron charge $q$ of $4.8 \times 10^{-10}$ esu, the Langevin rate constant $k_L$ would be equal to $2.12 \times 10^{-9}$. If the temperature of the drift tube is 70 °C (343 K) then the resulting value of x in equation 2.21 is 0.31. Plugging x=0.31 into equation 2.20 results in a reaction rate $K_{cap}$ equal to 1.04. Multiplying $k_L$ by $K_{cap}$ gives an estimated reaction rate constant of $2.20 \times 10^{-9}$. If we assume 100% transmission of toluene and the PTR-MS is operated at 80 Td with a drift pressure of 2.1 mbar and a drift voltage of 325 V then the number density of gas in the drift tube is $4.437 \times 10^{16}$ molecules cm$^{-3}$ and the electric field strength is 35 V cm$^{-1}$. Equation 2.18 can be simplified by substituting in the drift velocity:

$$ncps = 10^{-3} \times \frac{kLN}{V_d} \times \frac{T_{RH^+}}{T_{H_3O^+}}$$

(2.24)

Applying the above information into equation 2.24 will result in a theoretical sensitivity of 15.2 ncps for toluene. However, this sensitivity is an overestimation as the transmission of toluene is
not 100%. According to equation 2.23, the estimated relative transmission of toluene is 0.991, which results in a theoretical sensitivity of 15.1 ncps. The theoretical sensitivities at different drift conditions are summarized in Table 2.1.

Measuring Sensitivities

While theoretical sensitivities do provide valuable information, it is important to calibrate the instrument from known mixtures to assess the fidelity of the calculations. During the CARES campaign, a gas standard (Scott-Marrin) containing 12 compounds (listed in Table 2.2) and formaldehyde from a permeation tube (Kintek) were diluted with zero air generated by scrubbing humid air with a heated Pt catalyst. Reasonable agreement was observed at $m/z$ 93, 105, 107, and 121 corresponding with the peak of our transmission efficiency identified at $m/z$ 105. The measured sensitivity tends to be much larger than theoretical for the lighter ion. The cause is unclear and requires further investigation. The difference could be attributed to uncertainties in the drift tube concerning inaccurate quantification of the drift tube pressure, voltage, temperature, and length. Additionally, as explained earlier, the transmission efficiency detailed above requires further investigation.

2.1.3.5. Detection Limits and Measurement Error

The precision of the measurement is best described using Poisson counting statistics. In this manner, the standard deviation of the measurement is equal to the square root of the count rate. For example, if a 9 Hz ion count is observed, the standard deviation is $\sqrt{9}$ or 3 Hz. The detection limit (DL) can be calculated using the probability mass function for a Poisson distribution for the confidence interval of events $x$ occurring during a given time:

$$p(x, \lambda) = \frac{e^{-\lambda} \lambda^x}{x!}$$  \hspace{1cm} (2.25)
The function calculates the probability of the number of events occurring within x number of events based on the average number of events λ. For determining DLs of the PTR-MS, λ is the average number of background counts (events) occurring within the dwell time (s). If the DL is defined as the number of counts that occur outside of the 95% probability margin, then DL is when equation 25 equals 95% for the given x. For example, the average background count rate observed at m/z 93 during CARES was 4 Hz (λ). Solving equation 25 for x=7 and x=8 results in probabilities of 94% and 97% respectively. Since 8 Hz is the smallest number resulting in a probability of occurring above 95% this value is chosen as a representative detection limit.

Given a sensitivity of 17 ncps for m/z 93 and a H₃O⁺ count rate of 5 MHz, the 8 Hz DL count rate can be converted into a mixing ratio using equation 2.4.

\[
MR = \frac{SLg(R) - BKG(R)}{ncps(R) \times MHz H₃O^+} = \frac{8-4}{17 \times 5} = 0.047 \ ppbv
\] (2.4)

Table 2.3 is a summary of the PTR-MS detection limits of key species during CARES.

### 2.2. Description of IVOC Thermal Desorption Sampler

#### 2.2.1. Overview

This chapter details the development and construction of a sampling method to improve the quantification of IVOC abundance using a thermal desorption sampler integrated into a proton transfer reaction mass spectrometer (PTR-MS). The sampling approach is to alternate VOC sampling by the PTR-MS with analysis of heavier organics collected on a thermal desorption sampler. In this way, the abundance of IVOC compounds can be compared to the abundance of VOC compounds using the same principle of measurement. The PTR-MS identifies organics by molecular weight (MW, g mol⁻¹), hence isomers are lumped together, simplifying the analysis of complex mixtures and improving detection of larger organic...
compounds with many isomeric forms. The IVOC sampler is able to improve the detection limit of larger organics and provides a means to discriminate among VOC species.

The IVOC sampler was tested by sampling diesel and gasoline engine exhaust from inhalation exposure chambers at the Lovelace Respiratory Research Institute in Albuquerque, NM. The diesel engine was a 5.5 kW Yanmar diesel electric generator and the gasoline engine a 1996 model General Motors 4.3-L V-6 mounted to a dynamometer. The emissions from these engines and facility description are described in more detail in McDonald et al. (2004; 2007; 2011). The facility can blend diesel and gasoline engine exhaust in different proportions and thus provided an excellent opportunity to test the IVOC thermal desorption sampler. Over a series of tests, the engine load was varied and the exhaust diluted to different extents with clean, dry air. A portion of the diluted exhaust flow was diverted through a 1.5 m$^3$ exposure chamber from which the PTR-MS sampled. The inlet for the PTR-MS consisted of a heat traced electropolished steel tubing (UHP Cardinal) protected by a 1.0 µm Teflon particle filter that was replaced after each experiment.

Representative mass spectra of diesel and gasoline engine exhaust are shown in Figure 2.7. Ions are grouped and color coded by compound classes. The data were collected at 80 Td in VOC mode using a -30 °C dehumidifier as detailed in (Jobson and McCoskey, 2010) to remove water vapor and to some extent, depending on exhaust concentrations, lower volatility organics. Shown are ions measured in selective ion measuring mode of the PTR-MS and include major ions from the compound groups identified in diesel fuel plus ions attributed to oxygenated species known to be emitted in exhaust such as formaldehyde ($m/z$ 31), acetaldehyde ($m/z$ 45) and acetone + propanal ($m/z$ 59). The diesel engine was operated under a low engine load, the gasoline engine was under a typical engine load and both exhausts were diluted with similar
flows of dry air. For a similar level of dilution, gasoline exhaust displayed much higher concentrations of VOCs. For both engine types the major organic compounds in exhaust have been reported to be aldehydes, light alkenes and alkanes, and alkylbenzenes (Hoekman, 1992; Schauer et al., 1999; Schauer et al., 2002; Schmitz et al., 2000; Smith et al., 2002; Jobson et al., 2005). A large fraction of the mass emission rate is comprised of low molecular weight compounds with prominent peaks associated with aldehydes and ketones ($m/z$ 31, 45, 59, 73), light alkenes ($m/z$ 43, 57, 71), and alkylbenzenes ($m/z$ 79, 93, 107, 121, 135). The need for discrimination arises from the similarity of gasoline and diesel exhaust and the presence of alkenes, which respond at the same ions as alkanes.

Table 2.4 compares the percentage of ion signal found for selected ions within the different compound groups for the fuel and exhaust. For PTR-MS measurements of long chain alkanes and other IVOC species associated with engine exhaust in urban air, it will be necessary to both discriminate against the very abundant light alkenes which produce interfering ions for the measurement of IVOC alkanes and to preconcentrate the air sample to improve detection of the much lower abundant IVOC range species. For example, the ion signal for IVOC alkylbenzenes with carbon numbers of 10 or greater is about 2 orders of magnitude less than xylenes at $m/z$ 107. This need motivates thermal desorption sampling that can both discriminate against volatile alkenes and preconcentrate IVOC compounds. This chapter will describe technical details about the construction and operation of the sampler, interpretation of the desorption peaks, calibrations and sensitivity calculations, the background signals, the detection limits, and the discrimination technique.
2.2.2. Construction and Operation

Figure 2.8 shows a diagram of the thermal desorption sampler used to collect IVOC compounds. The PTR-MS drift tube has 2 inlets, one for the IVOC thermal desorption sampler and one for VOCs as described in Jobson and McCoskey (2010). The thermal desorption sampler used Tenax TA adsorbent resin, providing a means to preconcentrate organic compounds to improve detection, and to provide a means to discriminate against the collection of volatile organic compounds that can interfere in the interpretation of the PTR-MS mass spectrum. Approximately 0.175 grams of Tenax TA was packed into a 0.172 cm (0.0675”) ID stainless steel tube. The tube was resistively heated with an AC current and temperature controlled using a phase angle control module (Nu Wave Technologies) controlled by a proportional-integral-derivative (PID) algorithm. Mass flow controllers were used to regulate the sample, desorption, and back flush flows through the adsorbent. Dry nitrogen gas was used for desorption and back flush. The absorbent was plumbed into a 2-position six port gas sampling valve (VICI Valco). Another multi-position 4-port valve was used as a stream selector to sample ambient air or zero air (dry N\textsubscript{2}). The sampler was controlled by a software program (Azeotech DaqFactory) that allowed for automation of the sampling and thermal desorption steps. The thermal desorption sampler was connected to a custom made sample ring on the PTR-MS drift tube by a 0.0254 cm (0.01”) ID sulfinert stainless steel tube (Restek). The thermal desorption trap was positioned directly above the PTR-MS drift tube and electrically isolated from the sample drift ring. All sampling lines were either heat traced electropolished stainless steel tubing (UHP Cardinal) or silica coated stainless steel tubing (Sulfinert, Restek Corp). The setup allowed for easy switching between the VOC sampling and IVOC desorption sampling with minimal disruption of the drift tube pressure. While the IVOC sample is being collected,
the IVOC inlet is shut (S1 closed) and the VOC inlet is open (S2 open) to allow for VOC measurement. The VOC sample is dried by passing the sample through a -30 °C cold tube and the low abundance of H₂O vapor in both measurement modes allows for operation of the drift tube at 80 Townsends (Td) to reduce fragmentation.

The temperature of the Tenax adsorbent trap was thermostated to control sampling, purging, and desorption temperatures. The desorption temperature as measured inside the trap was 230 °C. The volume of air collected on the trap could be varied by controlling the sample collection time. Zero air was collected on the trap in the same manner as a sample and peak responses above the zero air signals were determined. Peak areas were integrated with custom analysis software (Wavemetrics IgorPro). The area under the desorption peak is proportional to the moles of analyte collected on the Tenax trap.

2.2.3. Plumbing Schematic and Components

The configuration and parts of the IVOC sampling system can be viewed in Figure 2.9 and Table 2.5. The Tenax adsorbent trap was subjected to four different temperature and flow conditions: sample, purge, measure, and backflush. Dry nitrogen was selected as the desorption gas during IVOC measurement since it allows for operation at 80 Td due to minimal amount of water vapor. This reduces the water clustering as well as O₂⁺ concentrations. During sample mode, the Tenax is thermostated to 30 °C and ambient air is pulled through the Tenax at 40 sccm. Once sampling is complete, the multiposition 4-port valve switches so that dry nitrogen gas is now pulled through the trap and the Tenax temperature is raised to 150 °C. The purpose of this “purge” mode is to remove volatile organic compounds such as alkenes and aldehydes that produce interfering ions in the measurement of higher molecular weight alkanes. The retention of a species within Tenax TA is characterized by its breakthrough volume.
breakthrough volume is described as the volume of air that must pass through the Tenax for the species to travel from beginning to end of the Tenax and effectively ‘breakthrough’ on the other side for a unit mass of the adsorbent material. The breakthrough volumes of toluene, octane, and dodecane are reduced to 11, 8.6, and 107 mL respectively at 150 °C for 0.175 g of Tenax. The amount of removal (discrimination) is determined by trap temperature and the volume of N\textsubscript{2} passed through the Tenax. During the Lovelace chamber experiments, a purge volume of 86 mL of dry nitrogen was used. Once purging is complete, the system switches into “measure” mode where the Tenax is heated to 230 °C and a dry nitrogen flow of 25 sccm is pushed through the Tenax into the PTR-MS drift tube. The trap is heated from 30 °C to 230 °C in 65 s. At this temperature the breakthrough volume of n-hexadecane (C\textsubscript{16}), n-pentacosane (C\textsubscript{25}), and n-hexacosane (C\textsubscript{26}) are 5, 71, and 168 mL respectively. A total desorption volume of 125 mL of nitrogen passes through the Tenax. This means there should be sufficient volume to desorb C\textsubscript{25} and lighter alkanes. With measurement complete, the system switches into a backflush mode to clean the Tenax to prevent carryover between measurements. During this time the Tenax is kept at 230 °C, but the dry nitrogen flow is increased to 100 sccm and flows in the opposite direction of the sample and measure modes. An additional 125 mL of gas is used to purge the Tenax. The sample, purge, measure, and backflush flows are controlled by a potentiometer (POT) located on the corresponding MFC control board.

2.2.4. Electrical Components

A schematic of the IVOC sampler electrical system can be viewed in Figure 2.10 and the parts are listed in Table 2.6. The IVOC system is outfitted with four solid state relays (SSRs) which are used to control the PTR-MS VOC system and the solenoid valves. All the valves have the same power requirements of 12 VDC and 1 amp. The solenoid valves are powered in
parallel by the IVOC box power supply, but the PTR-MS VOC system valve is powered from
the PTR-MS. The SSRs are from Opto 22 and are switched with 5 V logic from a Labjack U3
data acquisition / control device.

The power for the MFCs is handled differently than the rest of the system. They require
±15 VDC and 0.1 amps, which is provided from a DC/DC converter (Power-One). The
converter handles a range from 18 to 36 VDC and converts it to ±15 VDC and 0.7 amps. The
power is provided to the MFCs through custom control boards from Air Quality Design. These
boards provide control of the MFCs through a potentiometer that is used to set the 0-5 V control
signal to the MFCs.

The most complicated part of the electrical system lied with the Tenax trap heating.
Resistive heating using AC power was used to heat the trap. Trap temperature and heating rates
were controlled with a PID algorithm routine in Daq Factory. The PID algorithm controlled a
LabJack analog output (DAC0) to provide a variable voltage input for a solid state relay (SSR)
control module (Nu Wave Technologies). The SSR control module regulates an SSR connected
to a Hammond AC/AC power transformer (output 5 volts at 35 Amps) and the input signal to the
SSR control module had a linear relationship to the current output from the power transformer.
A higher current on the Tenax tube resulted in faster heating and a higher achievable
temperature. The power was routed through another SSR (Crydom) to allow for complete
shutoff of the heating. This offered automated shutoff of the heating system and could act as a
safety precaution to turn off the heat if excessive temperature levels were reached. This was
achieved through interaction with DaqFactory. The SSR was connected to the IVOC sampler
LabJack, so DaqFactory could control the SSR with a voltage of 5 V (On) or 0 V (Off).
2.2.5. Data Acquisition and Automation

The IVOC system was automated through the utilization of a LabJack U3 data acquisition and control hardware device and DaqFactory (AzeoTech) software. The LabJack U3 consisted of 16 ports that could be configured to be digital or analog inputs, or digital output. Access to 8 of these channels could be found as terminal connectors (FIO0-7) and 8 others are on a DB-15 connector (EIO0-7). To communicate with these channels in DaqFactory, the channel numbers correspond to 0-7 for FIO0-7 and 8-15 for EIO0-7. The DB-15 connection also contained 4 channels that were only digital in/out configurable (CIO0-3). The channel numbers for these correspond to 16-19 for CIO0-CIO3 within DaqFactory. Further details concerning the configuration of the LabJack and DaqFactory for the different channels can be found in Table 2.7. The function of each channel is explained further in the following section. The analog to digital channels (A to D) allowed DaqFactory to record the corresponding temperature, flows, and valve states. The digital output channels (Dig Out) allowed DaqFactory to switch valve states or turn on the Tenax heating system. The IVOC system was automated through the custom written sequences within DaqFactory, which used the Dig Out channels to switch valves and control Tenax heating at specified time intervals. The sequences used can be found in Appendix A. The Tenax heating technique also utilized an analog output channel (DAC0) and a DaqFactory PID loop to control the temperature, which is described in further detail below. A schematic of the Labjack connections to the different components is displayed in Figure 2.11 along with Table 2.8 detailing the various parts. Further explanation of the setup and communications can be found in Appendix B.

The operation of the IVOC system is performed through the use of a custom built interface within the DaqFactory software. This interface is displayed in Figure 2.12, which
allows for the user to define the times and temperatures of the different modes and observe the current status of the IVOC operation. The dials in the top left allow the user to set the sample, purge, measure, and backflush times and temperatures. This temperature corresponds to the temperatures measured from the thermocouple located on the outside of the Tenax tube. The temperature is maintained by a PID loop and the thermocouple on the outside of the tube. For reference, outside temperatures of 100, 120, 140, and 185 °C result in inside temperatures of 125, 150, 175, and 230 °C, meaning the inside temperature is approximately 25% higher than the outside temperature.

The buttons along the left side allow for manual switching of the valves, except the button controlling the inlet valve has been deactivated to prevent accidentally opening the valve during IVOC measure mode. If both the IVOC system and VOC inlets are opened at the same time, the drift pressure increases enough to trip a pressure interlock on the PTR-MS and power to the drift tube is turned off.

The IVOC operation is fully automated by a sequence that can be started with the ‘Begin IVOC’ button. As long as the times and temperatures are set the user does not have to do anything else for the system to run. The sequence will go through each mode once unless the ‘Keep Running?’ option is selected. As long as this option is toggled the IVOC system will run continuously. The ‘Zero?’ button allows the user to specify the IVOC system to run a zero on the next run. This is typically used in the laboratory setting when zeros can be performed at user discretion. During field campaigns, periodic automated zeros were coded into the operation sequence to ensure that there was a sufficient record of the background throughout the campaign.

The current gas flows, valve states, and temperatures are viewed through the flow diagram. The green arrows will light up to denote the direction of gas flow and depending on the
mode the lines will change from blue (sampling, purge, backflush) to red (measure), which corresponds to the valve state of the 6-port actuator: blue for state B and red for state A.

The interface also includes manual control over the heating elements. This is primarily to change the temperature quickly or stop the heating during an emergency. These buttons will generally not be utilized during normal operation as the automated sequence and other buttons on the interface manage these values. The ‘Tube Heating PID’ button turns on and off the PID loop controlling the Tenax temperature. The PID loop should begin automatically on startup and should always remain on. The ‘Enable Heat’ button controls an SSR on the power transformer and will stop Tenax heating. The automated sequence automatically changes this value, so this button should only be used if the user thinks there is a heating issue and needs to shut off the heating power. However, if such a scenario arises, the best procedure would be to turn off the power via the heating power switch on the back of the IVOC box. The ‘Temp_Control’ button is not actually a button, but acts as an indicator for how much power used for heating during a particular time. The ‘Set Temp to XX C’ buttons are used as a quick way to change the temperature, but are redundant due to the temperature options described previously. These buttons are for testing purposes and should be not be used during typical IVOC operation. The graph on the bottom right shows the real-time Tenax trap temperatures: inside (black) and outside (red).

2.2.6. Data Processing

The data processing was performed through custom programming functions written in WaveMetric’s IgorPro software. In order to ease the data handling process, a panel interface was developed that allows access to the important functions. This interface can be viewed in Figure 2.13. A user simply starts with the first button named ‘Prep Waves’ and continues down, hitting
each button in order. The functions will automatically produce tables and graphs to allow for quality assurance checks to assess that the functions are working properly. Further information on the functions can be found in annotated form in Appendix C. The processing of the IVOC sampler data requires a number of steps to transform the raw signal (Hz) into a mixing ratio (ppbv). With minimal user input, the custom written functions normalize all the data to MHz $m/z$ 21, identify and determine a base width for each ions measured thermal desorption peak, determine average values for background count rates for each ion, and lastly integrate the area response between the sample signal and the background signal for a given base width for each peak for each ion. The resulting areas can then be divided by the compounds sensitivity factor given in units of peak area counts nmol$^{-1}$ to yield nmol of compound. The nmol of compound is divided by the moles of air sampled to yield a mixing ratio (ppbv).

2.3. Performance and Characteristics of the Thermal Desorption Sampler

2.3.1. Desorption Peak Area

To determine the abundance of a compound using the IVOC thermal desorption sampler the resulting ion signal versus time trace “peak” must be integrated to get the total ion count. The total ion count is proportional to the moles of analyte desorbed from the trap. A Riemann sum approach is used to integrate the area under the desorption peak. The ion count rate (Hz) at each data point is multiplied by the measurement cycle time (s) resulting in an area in the units of counts, which will be referred to as area counts (AC). The sum of the area counts of all the cycles within the integration area results in the total desorption area counts. The window in Figure 2.14 shows an example of the area counts observed during each cycle. The beginning of the integration area is defined by the Tenax temperature begins to increase, corresponding to the vertical dashed line in the figure. Once the temperature begins to increase there is typically
significant analyte desorption. However, there can be a delayed desorption signal if the analyte has a large breakthrough volume. Under this scenario, the beginning of the integration area begins where the desorption signal is significantly different from the background (zero air) signal. An example of this is displayed in Figure 2.15 where the beginning of the integration area would correspond to cycle 19. Lab tests have shown that a signal one sigma above the zero is typically sufficient enough to capture a desorption area. The end of the integration area is defined when the signal decreases below this value, which corresponds to cycle 104 in Figure 2.15.

A typical desorption has the Tenax temperature increasing from 30 °C to 230 °C in approximately 65 s. The PID loop controlling the heating could be configured to allow for faster heating and sharper peaks, but this would have adverse effects on desorption peak shapes. The IVOC sampler quantifies a large range of species with very different desorption times. Based on breakthrough volumes, n-dodecane and hexadecane would desorb in 23 and 30 s respectively under the typical heating described above. If the Tenax heated from 30 °C to 230 °C in 30 s, the desorption times of n-dodecane and n-hexadecane would decrease to 11 and 15 s respectively. While this results in a better peak for n-hexadecane, the n-dodecane peak would shrink and a significant amount of signal would go unmeasured between measurement cycles. The measurement cycle time is typically around 6 seconds, so the desorption peaks would only contain 2 or 3 points under the 30 s heating time. By implementing a longer heating time, the IVOC sampler is able to capture more of the light species signal with minimal effect on the heavy species signal.
2.3.2. VOC-IVOC Comparison

Figure 2.16 shows an example of a typical thermal desorption peak from the trap. Shown is a time series of the 1,3,5-trimethylbenzene ion signal from a calibration gas test mixture. The test mixture was measured in VOC mode, passing through the -30 °C water trap, while a 257 cc air sample was simultaneously being collected on the Tenax trap over a sampling period of 6 minutes, as indicated by the shaded area under the trap flow rate in the figure. After sample collection, the trap was purged with dry N\textsubscript{2} for 4.5 minutes to remove traces of air, then the gas sampling valve was rotated to connect the trap to the drift tube. After 30 seconds of settling time the trap was heated to 230 °C in 65 seconds under a 25 sccm carrier N\textsubscript{2} flow. To demonstrate the trapping efficiency and equivalent sensitivity for the 2 modes, the area under the desorption peak (A2) can be shown to be equal to the area under the VOC trace (A1) accounting for the differences in air volume sampled. The product of IVOC sample collection time in seconds multiplied by the \textit{m/z} 121 normalized count rates in VOC mode yields area A1 of 50,000 counts. The air flow through the drift tube is 25 sccm corresponding to a 150 cm\textsuperscript{3} volume of air sampled into the drift over the IVOC sample collection time. The VOC air sample volume is thus 58% the size of the IVOC air sample volume. Multiplying the IVOC area A2 of 88,420 counts by the ratio of sample volumes yields an equivalent area of 51,600 counts, only 3% larger than area A1. The peak area A2 is determined from the start of the desorption heating time to when the ion signal reaches the background count rate. As in VOC mode, humid zero air is collected on the Tenax trap in the same manner as an air sample and desorbed to determine background area counts.
2.3.3. IVOC Sensitivities

As discussed in section 2.1.3.3, the VOC mode molar mixing ratio for some compound $R$ in nmol mol$^{-1}$ (ppbv) is determined from equation 2.4:

$$MR_{VOC} = \frac{Sig_{(R)} - BKG_{(R)}}{ncps_{(R)} \times MHz \ H_3O^+}$$  \hspace{1cm} (2.4)

where $Sig_{(R)}$ and $BKG_{(R)}$ are the measured and background ion count rates (Hz), and $ncps_{(R)}$ is the normalized sensitivity for the compound in units of Hz ppbv$^{-1}$ per MHz H$_3$O$^+$. For IVOC mode a similar relationship holds to convert peak areas to molar mixing ratios but this must account for the air volume sampled.

$$MR_{IVOC} = \left[ \frac{AC_{(R)} - bkgAC_{(R)}}{nAC_{(R)} \times MHz \ H_3O^+} \right] / \text{moles air sampled}$$  \hspace{1cm} (2.28)

where $AC_{(R)}$ represents the area under the sample ion peak, $bkgAC_{(R)}$ the background area, and $nAC_{(R)}$ is the sensitivity of the PTR-MS to the compound $R$ in units of area counts per nmol.

Since the drift tube kinetics don’t change between VOC and IVOC modes, the intrinsic sensitivities are the same, and $nAC$ sensitivities can be calculated from VOC sensitivities. For example, a nominal VOC sensitivity of 10 Hz ppbv$^{-1}$ per MHz H$_3$O$^+$ and a 25 sccm air sample flow into the drift tube yields an 80 Td nAC sensitivity value of $5.38 \times 10^5$ area counts nmol$^{-1}$ per MHz H$_3$O$^+$. The conversion is detailed with the following equations:

$$25 \, \text{sec air} \, \text{min}^{-1} = 0.417 \, \text{sec air} \, \text{s}^{-1} = \frac{0.417 \, \text{sec air}}{22.414 \, \text{mol air}} = 1.86 \times 10^{-5} \, \text{mol air} \, \text{s}^{-1}$$  \hspace{1cm} (2.29)

$$\frac{10 \, \text{Hz} \times \text{mol air}}{1.86 \times 10^{-5} \, \text{mol air} \, \text{s}} = 5.38 \times 10^5 \frac{AC}{nmol \times MHz \ H_3O^+}$$  \hspace{1cm} (2.30)

Table 2.9 is a summary VOC and IVOC sensitivities for some key species. The VOC sensitivities were determined from a calibration tank standard (Scott-Marrin) during the LRRI experiments and the IVOC mixing ratios were calculated using equation 2.28.
2.3.4. Dynamic Dilution Calibrations

Species with low vapor pressures are typically not very stable as compressed gas standards. For calibrating the PTR-MS response to IVOC species a dynamic dilution system was used based on a low flow syringe pump (Harvard Apparatus). The syringe pump was used to deliver low flow rates of a neat liquid into a dilution flow of air or nitrogen. Multiple syringes could be used so that a mixture of 2 or more compounds could be created by injecting the neat liquids. The needle of a 0.5 µL syringe pierced a septum on a stainless steel tee fitting. The liquid was evaporated from the tip of the syringe under the flow of the diluent gas. The manifold tee where the liquids were injected was temperature controlled between 30 and 80 °C. Downstream of the manifold the tubing was temperature controlled to 80 °C. The PTR-MS sub-sampled from this flow. It was observed that if the infusion rate was too low then evaporative loss from the needle of the syringe was greater than the infusion rate. To determine the accuracy of the dynamic dilution system, test mixtures of toluene, p-xylene, and 1,3,5-trimethylbenzene were made ranging from 1 ppbv to 1 ppmv by varying the infusion rate. These mixtures were sampled by the PTR-MS and the measured ion signal converted into a mixing ratio using calibrated response factors determined from a multicomponent VOC compressed gas standard containing these components (Scott-Marrin, accuracy ±5%). The measured molar mixing ratio was compared to that calculated from the infusion rate and molar flow of the diluent air. Measured mixing ratios agreed within 15% or better for mixing ratios > 10 ppbv, giving confidence that the system could reproducibly deliver reasonably accurate test mixtures for determining n-alkane sensitivities. For the n-alkane sensitivity tests, the injections were typically performed at 0.5 µl hr⁻¹ and diluted by 20 slpm of dry nitrogen resulting in a mixing ratio of approximately 40 ppbv for dodecane. The lowest mixing ratios achievable were dependent on
the compounds vapor pressure; lower vapor pressures allowed for lower syringe pump infusion rates. Gasoline and diesel fuel were also evaporated using this system to make test mixtures of the fuels for sampling by the PTR-MS.

2.3.5. IVOC Backgrounds

Dry nitrogen from a liquid N\textsubscript{2} dewar was used as a source gas to determine background (zero analyte) ion signals for the thermal desorption sampler. Periodic zeros are important to perform during both laboratory and field measurements to ensure that the background does not change or there is no carryover effects from previous runs. The PTR-MS IVOC sampler has been deployed in the field twice. The first deployment was during the Carbonaceous Aerosols and Radiative Effects Study (CARES) campaign in Sacramento, CA during April of 2010. The other deployment was during chamber experiments in May of 2012 at the Lovelace Respiratory Research Institute (LRRI) in Albuquerque, NM. During both campaigns periodic zeros were performed and they offer a good metric to see how much the zeros change at both short and long term time scales. Figure 2.17 shows a compilation of zeros for commonly observed ions m/z 57, 85, and 93. The units are in Hz normalized to MHz H\textsubscript{3}O\textsuperscript{+}. There were more zeros performed during CARES (n=38) than LRRI (n=22) due to the differences in sampling duration. CARES was continuous monitoring over a long period, which allowed for periodic zeros every 4 hours. The LRRI experiment was more time constrained and experiments were only performed during working hours, which resulted in a more limited time to perform zeros. The major differences between the two different experiments are the dwell times and the purging temperatures used. The dwell times during LRRI (50 ms) were a factor of 4 smaller than CARES (200 ms), which will result in a higher level of noise for LRRI relative to CARES. The purge temperature has an
effect on select \( m/z \) zeros and during CARES the purge temperature was much lower than the purge temperature during LRRI. This difference is explained in more detail in below.

Given all the differences, the zeros have not changed significantly over roughly a two year span. The average ion count rate and standard deviation of the zeros are quite similar, with the variability of the LRRI zeros attributed to the smaller number of zeros being averaged and the smaller dwell times. The zeros during CARES due seem a bit higher, which is most apparent with the \( m/z \) 93 zero. These differences may be attributed to the different purge temperatures and techniques.

For a majority of the \( m/z \) ions, the zeros were similar under varying purge temperatures. This is displayed in the bottom panel of Figure 2.18. The purge temperatures were 30, 125, and 150 °C. Looking at the figure, all of these zeros are close to the average zero and the little variability observed is within one sigma of the average. Conversely, there were a few key species with purge temperature dependent zeros (\( m/z \) 57, 83, 85, 87, 93, 101, 105). One of the more extreme cases lies at \( m/z \) 93. Under the 30 °C purge, there is a large response. This response is decreased at the 125 °C purge temp and is essentially nonexistent at the 150 °C purge. With this in mind, running the purge at higher temperatures (150 °C) will reduce the background signal and allow for lower detection limits. It is suspected that the high backgrounds observed after the lower purge temperatures is a result of contamination. The source likely lies with carryover from the backflush or contamination during zero sampling. The backflush flow is controlled with a MFC, which can often be contaminated. During the end of the backflush mode, the heating is turned off, but nitrogen is still flowed through the Tenax to aid in cooling of the trap back to ambient temperature. It is during this time that contamination from the MFC would be accumulated on the Tenax, which shows up during the next desorption unless
discriminated against. During zero air sampling, contamination along the lines, needle valves, or MFCs used would be accumulated on the Tenax. Operating the IVOC sampler at a 150 °C purge temperature is recommended as it effectively eliminates this contamination.

2.3.6. IVOC Detection Limits and Measurement Error

The detection limits of the IVOC system were determined from periodic zeros in Figure 2.17 performed during CARES. On average, the base width of the desorption peaks was approximately 120 s. Using this base width, the area counts for all zeros (n=38) at each ion were calculated and averaged. The signal was normalized to MHz H$_3$O$^+$ before calculation of the area counts. The detection limit was defined as three times the standard deviation (3σ) of this average area counts. The 3σ area counts were converted into a mixing ratio by dividing by the IVOC sensitivity (AC nmol$^{-1}$) and dividing by the moles of air sampled. For example, if a 1 L air sample was collected, toluene (m/z 93) had an IVOC sensitivity of 1.13x10$^6$ AC nmol$^{-1}$, and 3σ was 1387 AC, the detection limit of toluene would be 1.5 pptv. This detection limit is well below the VOC detection limit of 54 pptv for toluene (Sec 2.1.3.5), showing that the IVOC system can greatly decrease detection limits. The detection limit for alkanes was calculated to be 44 pptv, which could be decreased further by increasing sample time. Table 2.10 lists the detection limits of the ions measured in IVOC mode during CARES.

2.3.7. IVOC Sampler Discrimination

2.3.7.1. Breakthrough Volumes and Theoretical Discrimination

The trapping efficiency of a compound by an absorbent resin like Tenax is expressed as a breakthrough volume. As stated previously, a breakthrough volume is described as the volume of air that must pass through the Tenax for the species to travel from beginning to end of the Tenax and effectively ‘breakthrough’ on the other side for a unit mass of the adsorbent material.
The generic breakthrough volume of Tenax TA is typically expressed as liters of air per gram of Tenax and this varies greatly between compounds. A summary of breakthrough volumes in units of \( \text{L}_{\text{air}} \text{ g}^{-1} \) is provided by Scientific Instrument Services (SIS, 2012), but the breakthrough volumes of key compounds within the IVOC sampler is detailed in Table 2.11. These breakthrough volumes were calculated based on the data provided by Scientific Instrument Services and multiplying these values by the mass of the Tenax TA in the IVOC sampler (0.175 g), which were then plotted and fit with a LogNormal regression fit to allow for estimation of the breakthrough volume at any temperature. When a calibration standard is not available for a species, the breakthrough volume can be used to estimate a theoretical discrimination by comparing it to species with a characterized discrimination.

In the operation of the IVOC sampler, the purge mode was enabled for a total of four minutes. For the first two minutes, the trap temperature increases to the set-point temperature and is held constant. Trap heating is then turned off and the trap cools for the last two minutes while still flushing the Tenax with dry nitrogen. The purge volume is considered the volume that flushes through the Tenax when the temperature is raised, which results in an 86 mL purge volume. Any species with a breakthrough volume lower than this should be removed. These species are identified in bold type in Table 2.11. Operating the purge mode at 150 °C will allow for discrimination against VOC alkenes and alkanes (\( < \text{C}_{12} \)). During IVOC measurement, ~125 mL is flowed through the Tenax. Desorption at 230 °C should allow the complete desorption and measurement of species up to \( \text{C}_{25} \).

2.3.7.2. Observed Discrimination of Individual Compounds

Figure 2.19 shows the desorption peaks of compounds with varying Tenax breakthrough volumes. Methacrolein, benzene, toluene, p-xylene, 1,2,4-trimethylbenzene, 1,2,3,5-
tetramethylbenzene, the C\textsubscript{9} to C\textsubscript{13} n-alkanes and pentadecane were subjected to two purge temperatures, 30 °C and 150 °C. The methacrolein and alkylbenzene mixtures were generated from a calibration standard tank (Scott-Marrin) and diluted with dry nitrogen. The n-alkane concentrations were generated using the dynamic dilution system with an infusion rate of 10 µL hr\textsuperscript{-1} of neat solutions. Each scenario allowed for a different degree of discrimination. Under the 30 °C scenario the volume of gas passes through the Tenax does not exceed the breakthrough volume of any of the six compounds, so no discrimination would be expected. This is represented by the blue trace in Figure 2.19. Conversely, under other purge temperatures the breakthrough volumes of all the compounds are significantly reduced, which will result in large discrimination against the VOCs. The 150 °C purge temperature scenario is represented by the red trace. Large discrimination against the lighter VOCs can be observed with the methacrolein, benzene and toluene signals decreasing by 98±7%, 99±5% and 97±5% respectively. Toluene and octane have similar desorption volumes, if toluene is purged octane would be purged as well. Approximately 90% of alkanes in gasoline fuel (Hoekman, 1992; Gentner, 2012) and 99% of alkanes in gasoline exhaust (Schauer et al., 2002) are octane or lighter. Calculations of the breakthrough volumes provides insight into what species would be removed during desorption.

The calculated breakthrough volumes of toluene, p-xylene, and 1,3,5-trimethylbenzene for the IVOC system at 150 °C are 11, 23.6, and 44.3 mL respectively. Even though there is sufficient volume flushed through the Tenax (86 mL), there is not 100% removal of the p-xylene and 1,3,5-trimethylbenzene. The breakthrough volume of decane, dodecane, and pentadecane at 150 °C are 32, 107, and 508 mL respectively. A purge volume of the 86 mL resulted in 86% removal of decane and 52% removal of dodecane. This results in retention of some heavy VOC alkanes (C\textsubscript{9} to C\textsubscript{11}) and some loss of light IVOC alkanes (C\textsubscript{12} and C\textsubscript{13}), but the removal rate is
nearly negligible for the heavier IVOCs with only 7.5% removal observed for pentadecane. Figure 2.20 shows the observed removal percentage versus the calculated breakthrough volume for n-alkanes from prepared test mixtures and alkylbenzene compounds observed in diesel engine exhaust experiments at LRRI and the multi-component compressed gas standard (Scott-Marrin) used to calibrate instrument response.

Looking at the n-alkane trend, complete removal of $C_8$ and lighter alkanes is achieved with minimal losses to IVOC species. The trend would lead to negligible removal of the $C_{16}$ to $C_{18}$ IVOC alkanes, minimal removal of $C_{14}$ and $C_{15}$ alkanes, and some loss of $C_{12}$ and $C_{13}$ alkanes. The $C_9$ to $C_{11}$ species will result in a degree of VOC alkane interference. According to Schauer et al. (2002), ~99% of gasoline exhaust non-methane alkanes are $C_8$ and lighter. Therefore, the purge mode should discriminate against gasoline alkanes, eliminating or vastly reducing their interference.

Since the diesel fuel has a large composition of alkylbenzenes, the observed removal rate at $m/z$ 79, 93, 107, 121, and 135 should reflect that observed with a gas standard. The bottom panel in Figure 2.20 shows good agreement in removal rates observed between #2 diesel fuel and a calibration gas standard (Scott-Marrin). There seems to be small differences observed at $m/z$ 79, 93, and 135. The difference at $m/z$ 79 and 93 may be attributed to fragmentation of larger aromatics to these ions, which would increase the response and lead to less observed removal. The trend lines in Figure 2.20 allow for trap losses of other compounds to be determined from the published breakthrough volumes.

This same discrimination also works to reduce the interference from alkene species. The Tenax TA breakthrough volumes for alkenes are very similar to the corresponding n-alkanes. For example, the breakthrough of 1-nonene is in between those observed for n-octane and n-
nonane. Therefore, under the 150 °C purge temperature the C₈ alkenes and lighter are removed, with some removal of the C₉ to C₁₁ alkenes. Light alkenes (C₂-C₆) are a major component of vehicle exhaust and are thus abundant in urban air (Lough et al., 2005; Schauer et al., 2009; Lai et al., 2004). Laboratory test have shown that at 80 Td light alkenes (propene, butenes) respond at the typical M+1 ion, but fragmentation occurs for heavier alkenes. By discriminating against the alkenes their interference at the lower CₙH₂ₙ₊₁ ions will be eliminated. The literature has not reported the presence of many alkenes larger than 1-nonene, so it is likely the 150 °C trap purge removes the major interfering alkenes ions (m/z 43, 57, 71, 85, 99) found in exhaust and urban air.

2.3.7.3. Vehicle Exhaust Discrimination Experiments

Although the discrimination against a calibration gas standard has been characterized, it is still important to characterize the discrimination of a complex mixture like diesel exhaust. Figure 2.21 shows mixing ratios of major species measured in gasoline and diesel engine exhaust using the IVOC sampler with different trap purge temperatures. The figure compares the IVOC data to the VOC mode data to reveal compound losses from the trap purge. The first thing to compare is the VOC mixing ratio versus the IVOC mixing ratio at 30 °C purge. For both diesel and gasoline exhaust, most of the IVOC 30 °C mixing ratios are within a factor of two of the VOC mixing ratios.

The IVOC system utilized operated purge mode at 30, 125, 150, and 175 °C. As described previously, the 150 °C purge scenario offered the best balance between maintaining IVOC species while removing VOC species. Under this scenario, large discrimination against gasoline exhaust is expected while the diesel exhaust species should show a much higher retention. Table 2.12 summarizes the removal between the 30 °C and 150 °C purge
temperatures. As expected, the gasoline exhaust experiences extensive removal with cycloalkanes and aldehydes \((m/z 83, 97, 111, 125, 139)\) and the light monoaromatics \((m/z 79, 93, 107, 121)\) showing > 90% reduction in ion signal for some compounds. The remaining signal at these light \(m/z\) values (i.e. 79, 93) is likely due to fragmentation of larger species. There was extensive loss observed at the alkane and alkene ions \((m/z 57, 71, 85, 99, 113)\). Both exhausts experienced much less removal for larger \(m/z\) values, reflecting the presence of low volatility, higher molecular weight compounds.

Approximately 37% of gasoline exhaust is composed of alkanes and approximately 22% of alkenes. Of these, only 59% of the alkanes (31% overall composition) and 41% of the alkenes (22% overall composition) are detectable by the PTR-MS. After discrimination, the detectable alkanes drop to less than 0.3% (less than 0.15% of overall composition) and there are no detectable alkenes. Table 2.12 shows that 97% of the alkane and alkene ion signal was removed by the 150 °C purge. This is a high level of discrimination, but >99% discrimination would be expected. The cause is unclear, but there could be more IVOC alkanes present in gasoline exhaust in this experiment than expected from reported literature.

Approximately 8% of diesel exhaust is composed of alkanes and approximately 4% of alkenes. Of these, 82% of the alkanes (48% overall composition) and 18% of the alkenes (10% overall composition) are detectable. After discrimination, the detectable alkanes dropped to 21% (12% of overall composition) and there are no detectable alkenes. In Table 2.12, the diesel exhaust ion signal attributable to alkanes and alkenes was reduced by 93% with the 150 °C purge. The remaining ion signal is attributed to IVOC alkanes. This is much more removal than expected, but this difference may be attributed to the large difference in sensitivities between the alkanes and alkenes. The alkenes are approximately 4 times more sensitive than the alkanes, so
their removal will have a much larger impact on the change in ion signal, resulting in an overestimation of removal.
2.4. References


### 2.5. Tables and Figures

Table 2.1: Theoretical and transmission efficiency corrected sensitivities of select species. The transmission efficiency (TE) is based off of equation 23, which assumes 100% transmission at m/z 105.

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<tr>
<td>80</td>
<td>pyridine</td>
<td>8.00</td>
<td>2.19</td>
<td>3.08E-09</td>
<td>21.3</td>
<td>0.94</td>
<td>20.0</td>
</tr>
<tr>
<td>93</td>
<td>toluene</td>
<td>12.90</td>
<td>0.343</td>
<td>2.20E-09</td>
<td>15.2</td>
<td>0.99</td>
<td>15.1</td>
</tr>
<tr>
<td>95</td>
<td>phenol</td>
<td>11.73</td>
<td>1.335</td>
<td>2.57E-09</td>
<td>17.8</td>
<td>1.0</td>
<td>17.7</td>
</tr>
<tr>
<td>105</td>
<td>styrene</td>
<td>15.86</td>
<td>0.186</td>
<td>2.37E-09</td>
<td>16.3</td>
<td>1.0</td>
<td>16.3</td>
</tr>
<tr>
<td>107</td>
<td>m-xylene</td>
<td>15.03</td>
<td>0.271</td>
<td>2.32E-09</td>
<td>16.0</td>
<td>1.0</td>
<td>16.0</td>
</tr>
<tr>
<td>107</td>
<td>p-xylene</td>
<td>15.08</td>
<td>0.081</td>
<td>2.28E-09</td>
<td>15.8</td>
<td>1.0</td>
<td>15.7</td>
</tr>
<tr>
<td>107</td>
<td>o-xylene</td>
<td>14.99</td>
<td>0.582</td>
<td>2.42E-09</td>
<td>16.7</td>
<td>1.0</td>
<td>16.6</td>
</tr>
<tr>
<td>107</td>
<td>ethylbenzene</td>
<td>14.85</td>
<td>0.297</td>
<td>2.32E-09</td>
<td>16.0</td>
<td>1.0</td>
<td>16.0</td>
</tr>
<tr>
<td>109</td>
<td>o-cresol</td>
<td>13.83</td>
<td>1.045</td>
<td>2.53E-09</td>
<td>17.5</td>
<td>1.0</td>
<td>17.4</td>
</tr>
<tr>
<td>109</td>
<td>m-cresol</td>
<td>13.83</td>
<td>1.033</td>
<td>2.52E-09</td>
<td>17.4</td>
<td>1.0</td>
<td>17.3</td>
</tr>
<tr>
<td>109</td>
<td>p-cresol</td>
<td>13.89</td>
<td>1.301</td>
<td>2.67E-09</td>
<td>18.5</td>
<td>1.0</td>
<td>18.4</td>
</tr>
<tr>
<td>121</td>
<td>123-TMB</td>
<td>17.09</td>
<td>0.66</td>
<td>2.57E-09</td>
<td>17.8</td>
<td>1.0</td>
<td>17.0</td>
</tr>
<tr>
<td>121</td>
<td>124-TMB</td>
<td>17.17</td>
<td>0.291</td>
<td>2.46E-09</td>
<td>17.0</td>
<td>1.0</td>
<td>16.3</td>
</tr>
<tr>
<td>124</td>
<td>nitrobenzene</td>
<td>13.25</td>
<td>4.68</td>
<td>5.49E-09</td>
<td>37.9</td>
<td>0.9</td>
<td>35.7</td>
</tr>
<tr>
<td>129</td>
<td>naphthalene</td>
<td>20.18</td>
<td>0</td>
<td>2.59E-09</td>
<td>17.9</td>
<td>0.9</td>
<td>16.3</td>
</tr>
<tr>
<td>137</td>
<td>a-pinene</td>
<td>18.07</td>
<td>0.149</td>
<td>2.47E-09</td>
<td>17.0</td>
<td>0.9</td>
<td>14.5</td>
</tr>
<tr>
<td>143</td>
<td>1-Methylnaphthalene</td>
<td>22.31</td>
<td>0.318</td>
<td>2.79E-09</td>
<td>19.3</td>
<td>0.8</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-------------------</td>
<td>-------</td>
<td>-------</td>
<td>------</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>143</td>
<td>2-methylnaphthalene</td>
<td>22.52</td>
<td>0.443</td>
<td>2.84E-09</td>
<td>19.6</td>
<td>0.8</td>
<td>15.6</td>
</tr>
<tr>
<td>169</td>
<td>dibenzofuran</td>
<td>20.00</td>
<td>1</td>
<td>2.84E-09</td>
<td>19.6</td>
<td>0.5</td>
<td>9.0</td>
</tr>
<tr>
<td>179</td>
<td>anthracene</td>
<td>29.30</td>
<td>0</td>
<td>3.06E-09</td>
<td>21.1</td>
<td>0.3</td>
<td>6.1</td>
</tr>
</tbody>
</table>
Table 2.2: The sensitivities measured during CARES compared to theoretical (Theo) calculations of sensitivity (equation 2.24) assuming 100% transmission and the theoretical sensitivity accounting for transmission efficiency (TE Theo) using equation 2.23.

<table>
<thead>
<tr>
<th>m/z</th>
<th>species</th>
<th>CARES (ncps)</th>
<th>Theo (ncps)</th>
<th>CARES / Theo</th>
<th>TE corrected Theo NCPS</th>
<th>CARES / TE Theo</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>formaldehyde</td>
<td>22</td>
<td>20.6</td>
<td>1.07</td>
<td>8.2</td>
<td>2.7</td>
</tr>
<tr>
<td>33</td>
<td>methanol</td>
<td>23</td>
<td>16.8</td>
<td>1.37</td>
<td>7.2</td>
<td>3.2</td>
</tr>
<tr>
<td>42</td>
<td>acetonitrile</td>
<td>39</td>
<td>32.4</td>
<td>1.20</td>
<td>18.4</td>
<td>2.1</td>
</tr>
<tr>
<td>45</td>
<td>acetaldehyde</td>
<td>30</td>
<td>23.9</td>
<td>1.25</td>
<td>14.6</td>
<td>2.1</td>
</tr>
<tr>
<td>59</td>
<td>acetone</td>
<td>33</td>
<td>21.7</td>
<td>1.52</td>
<td>16.9</td>
<td>2.0</td>
</tr>
<tr>
<td>69</td>
<td>isoprene</td>
<td>21</td>
<td>13.8</td>
<td>1.52</td>
<td>12</td>
<td>1.8</td>
</tr>
<tr>
<td>71</td>
<td>MACR</td>
<td>18</td>
<td>25.7</td>
<td>0.70</td>
<td>24.8</td>
<td>0.7</td>
</tr>
<tr>
<td>73</td>
<td>2-butane</td>
<td>40</td>
<td>25.1</td>
<td>1.59</td>
<td>22.6</td>
<td>1.8</td>
</tr>
<tr>
<td>79</td>
<td>benzene</td>
<td>17</td>
<td>13.6</td>
<td>1.25</td>
<td>12.7</td>
<td>1.3</td>
</tr>
<tr>
<td>93</td>
<td>toluene</td>
<td>17</td>
<td>15.2</td>
<td>1.12</td>
<td>15.1</td>
<td>1.1</td>
</tr>
<tr>
<td>105</td>
<td>styrene</td>
<td>18</td>
<td>16.3</td>
<td>1.10</td>
<td>16.3</td>
<td>1.1</td>
</tr>
<tr>
<td>107</td>
<td>p-xylene</td>
<td>16</td>
<td>15.8</td>
<td>1.02</td>
<td>15.7</td>
<td>1.0</td>
</tr>
<tr>
<td>121</td>
<td>124-TMB</td>
<td>14</td>
<td>17.0</td>
<td>0.82</td>
<td>16.3</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Table 2.3: CARES detection limits of key species during PTR-MS VOC measurements. The average H$_3$O$^+$ count rates were 4.69 MHz.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Species</th>
<th>BKG (Hz)</th>
<th>ncps</th>
<th>Detection Limit (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>formaldehyde</td>
<td>55.0</td>
<td>22</td>
<td>0.029</td>
</tr>
<tr>
<td>42</td>
<td>acetonitrile</td>
<td>5.1</td>
<td>39</td>
<td>0.021</td>
</tr>
<tr>
<td>45</td>
<td>acetaldehyde</td>
<td>50.8</td>
<td>30</td>
<td>0.023</td>
</tr>
<tr>
<td>59</td>
<td>acetone</td>
<td>22.7</td>
<td>33</td>
<td>0.034</td>
</tr>
<tr>
<td>69</td>
<td>isoprene</td>
<td>2.4</td>
<td>21</td>
<td>0.016</td>
</tr>
<tr>
<td>71</td>
<td>methacrolein</td>
<td>6.2</td>
<td>18</td>
<td>0.045</td>
</tr>
<tr>
<td>73</td>
<td>methyl ethyl ketone</td>
<td>14.7</td>
<td>40</td>
<td>0.028</td>
</tr>
<tr>
<td>79</td>
<td>benzene</td>
<td>3.4</td>
<td>17</td>
<td>0.033</td>
</tr>
<tr>
<td>93</td>
<td>toluene</td>
<td>3.7</td>
<td>17</td>
<td>0.054</td>
</tr>
<tr>
<td>105</td>
<td>styrene</td>
<td>1.9</td>
<td>18</td>
<td>0.036</td>
</tr>
<tr>
<td>107</td>
<td>p-xylene</td>
<td>2.2</td>
<td>16</td>
<td>0.037</td>
</tr>
<tr>
<td>121</td>
<td>1,2,4-trimethylbenzene</td>
<td>2.6</td>
<td>14</td>
<td>0.051</td>
</tr>
<tr>
<td>135</td>
<td>1,2,3,5-tetramethylbenzene</td>
<td>0.6</td>
<td>13</td>
<td>0.055</td>
</tr>
<tr>
<td>137</td>
<td>alpha pinene</td>
<td>0.5</td>
<td>6</td>
<td>0.124</td>
</tr>
</tbody>
</table>
Table 2.4: Comparison of Gasoline and Diesel Exhaust Composition at 80 Td.

<table>
<thead>
<tr>
<th>Group</th>
<th>Formula</th>
<th>Measured m/z</th>
<th>Diesel Exhaust</th>
<th>Gasoline Exhaust</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygenated alkanes and alkenes</td>
<td>C_{n}H_{2n+1}</td>
<td>31, 33, 45, 47, 59</td>
<td>50.3%</td>
<td>51.1%</td>
</tr>
<tr>
<td>cycloalkanes</td>
<td>C_{n}H_{2n-1}</td>
<td>43, 57, 71, 85, 99, 113, 127</td>
<td>19.4%</td>
<td>16.4%</td>
</tr>
<tr>
<td>alkylbenzenes</td>
<td>C_{n+6}H_{2n+7}</td>
<td>69, 83, 97, 111, 125, 139</td>
<td>4.3%</td>
<td>3.3%</td>
</tr>
<tr>
<td>unknown (bicycloalkanes)</td>
<td>C_{n+5}H_{2n+7}</td>
<td>79, 93, 107, 121, 135, 149, 163, 177, 191</td>
<td>22.3%</td>
<td>26.6%</td>
</tr>
<tr>
<td>naphthenic monoaromatics</td>
<td>C_{n+9}H_{2n+11}</td>
<td>119, 133, 147, 161, 175, 189</td>
<td>0.9%</td>
<td>1.0%</td>
</tr>
<tr>
<td>naphthalenes</td>
<td>C_{n+10}H_{2n+9}</td>
<td>129, 143, 157, 171</td>
<td>0.3%</td>
<td>0.3%</td>
</tr>
</tbody>
</table>
Table 2.5: List of parts of the IVOC sampling system.

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
<th>Company</th>
<th>Part #</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500 sccm Mass Flow Controller</td>
<td>MKS</td>
<td>1179A01352CS1BV</td>
</tr>
<tr>
<td>2</td>
<td>1000 sccm Mass Flow Controller</td>
<td>MKS</td>
<td>1179A01313CS1BV</td>
</tr>
<tr>
<td>3</td>
<td>50 sccm Mass Flow Controller</td>
<td>MKS</td>
<td>1179A01351CS1BV</td>
</tr>
<tr>
<td>4</td>
<td>Two Position Microelectric Valve Actuator</td>
<td>Vici Valco Instruments Co. Inc.</td>
<td>EDMA</td>
</tr>
<tr>
<td>5</td>
<td>Multi-position Electric Actuator</td>
<td>Vici Valco Instruments Co. Inc.</td>
<td>E4</td>
</tr>
<tr>
<td>6</td>
<td>Tenax Trap</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Diaphram Pump</td>
<td>Gast</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2-Way Normally Closed Soleniod Valve</td>
<td>Parker</td>
<td>009-0270-900</td>
</tr>
<tr>
<td>9</td>
<td>3-Way Soleniod Valve</td>
<td>Parker</td>
<td>009-0269-900</td>
</tr>
</tbody>
</table>
Table 2.6: Table of the electrical parts of the IVOC sampler.

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
<th>Company</th>
<th>Part #</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Power Switches</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Power Supply</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Terminal Board</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Solid State Relay and G4 4-Channel SSR Module Rack</td>
<td>Opto 22</td>
<td>G4ODC5</td>
</tr>
<tr>
<td>5</td>
<td>2-Way Normally Closed Solenoid Valve</td>
<td>Parker</td>
<td>009-0270-900</td>
</tr>
<tr>
<td>6</td>
<td>3-Way Solenoid Valve</td>
<td>Parker</td>
<td>009-0269-900</td>
</tr>
<tr>
<td>7</td>
<td>DC/DC Converter</td>
<td>Power-One</td>
<td>DFA20E24D15</td>
</tr>
<tr>
<td>8</td>
<td>MFC Control Board</td>
<td>Air Quality Design</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>500 sccm Mass Flow Controller</td>
<td>MKS</td>
<td>1179A01352CS1BV</td>
</tr>
<tr>
<td>10</td>
<td>1000 sccm Mass Flow Controller</td>
<td>MKS</td>
<td>1179A01313CS1BV</td>
</tr>
<tr>
<td>11</td>
<td>50 sccm Mass Flow Controller</td>
<td>MKS</td>
<td>1179A01351CS1BV</td>
</tr>
<tr>
<td>12</td>
<td>Solid State Relay Control Module</td>
<td>Nu Wave Technologies</td>
<td>SSRMAN-1P-HR</td>
</tr>
<tr>
<td>13</td>
<td>PCB Plug-In Transformer</td>
<td>DB Lectro Inc</td>
<td>TL77-4F-24</td>
</tr>
<tr>
<td>14</td>
<td>Power Transformer</td>
<td>Hammond</td>
<td>185G10</td>
</tr>
<tr>
<td>15</td>
<td>Solid State Relay</td>
<td>Crydom</td>
<td>D2W203F</td>
</tr>
</tbody>
</table>
Table 2.7: DaqFactory Channel Configuration for IVOC sampler.

<table>
<thead>
<tr>
<th>Channel Name</th>
<th>Ch. #</th>
<th>LabJack Port</th>
<th>LabJack DB15 Pin</th>
<th>I/O Type</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp</td>
<td>0</td>
<td>FIO0</td>
<td></td>
<td>A to D</td>
<td>Measures temperature inside Tenax tube</td>
</tr>
<tr>
<td>Temp_Backup</td>
<td>1</td>
<td>FIO1</td>
<td></td>
<td>A to D</td>
<td>Measures temperature outside Tenax tube</td>
</tr>
<tr>
<td>Read_TW_A</td>
<td>2</td>
<td>FIO2</td>
<td></td>
<td>A to D</td>
<td>Monitors signal when 2-position actuator is in position A</td>
</tr>
<tr>
<td>Read_TW_B</td>
<td>3</td>
<td>FIO3</td>
<td></td>
<td>A to D</td>
<td>Monitors signal when 2-position actuator is in position B</td>
</tr>
<tr>
<td>IVOC_Mode</td>
<td>4</td>
<td>FIO4</td>
<td></td>
<td>A to D</td>
<td>Monitors signal from PTR-MS to determine when to start Tenax desorption</td>
</tr>
<tr>
<td>MFC_Sample</td>
<td>5</td>
<td>FIO5</td>
<td></td>
<td>A to D</td>
<td>Records the sample flow</td>
</tr>
<tr>
<td>MFC_BF</td>
<td>6</td>
<td>FIO6</td>
<td></td>
<td>A to D</td>
<td>Records the backflush flow</td>
</tr>
<tr>
<td>MFC_Carrier</td>
<td>7</td>
<td>FIO7</td>
<td></td>
<td>A to D</td>
<td>Records the desorption flow</td>
</tr>
<tr>
<td>Valve_Carrier</td>
<td>8</td>
<td>EIO0</td>
<td>4</td>
<td>Dig Out</td>
<td>Toggles desorption valve</td>
</tr>
<tr>
<td>Valve_BF</td>
<td>9</td>
<td>EIO1</td>
<td>12</td>
<td>Dig Out</td>
<td>Toggles backflush valve</td>
</tr>
<tr>
<td>Valve_Inlet</td>
<td>10</td>
<td>EIO2</td>
<td>5</td>
<td>Dig Out</td>
<td>Toggles PTR-MS inlet valve</td>
</tr>
<tr>
<td>Valve_Sample</td>
<td>11</td>
<td>EIO3</td>
<td>13</td>
<td>Dig Out</td>
<td>Toggles sample valve</td>
</tr>
<tr>
<td>Valve_TW_B</td>
<td>12</td>
<td>EIO4</td>
<td>6</td>
<td>Dig Out</td>
<td>Switches 2-position actuator to position B</td>
</tr>
<tr>
<td>Valve_TW_A</td>
<td>13</td>
<td>EIO5</td>
<td>14</td>
<td>Dig Out</td>
<td>Switches 2-position actuator to position A</td>
</tr>
<tr>
<td>Valve_CZ_Step</td>
<td>14</td>
<td>EIO6</td>
<td>7</td>
<td>Dig Out</td>
<td>Rotates the multi-position actuator to the next port</td>
</tr>
<tr>
<td>Valve_CZ_Home</td>
<td>15</td>
<td>EIO7</td>
<td>15</td>
<td>Dig Out</td>
<td>Returns the multi-position to the ‘home’ position (port 1)</td>
</tr>
<tr>
<td>Heat_Enable</td>
<td>18</td>
<td>CIO2</td>
<td>10</td>
<td>Dig Out</td>
<td>Toggles the Tenax heating</td>
</tr>
<tr>
<td>Temp_Control</td>
<td>0</td>
<td>DAC0</td>
<td></td>
<td>D to A</td>
<td>Communicates to the SSR control module and the Tenax heating PID loop to control Tenax temperature</td>
</tr>
</tbody>
</table>
Table 2.8: Parts used for automation of the IVOC sampler.

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
<th>Company</th>
<th>Part #</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solid State Relay</td>
<td>Opto 22</td>
<td>G4ODC5</td>
</tr>
<tr>
<td>2</td>
<td>Solid State Relay</td>
<td>Opto 22</td>
<td>G4ODC5</td>
</tr>
<tr>
<td>3</td>
<td>Solid State Relay</td>
<td>Opto 22</td>
<td>G4ODC5</td>
</tr>
<tr>
<td>4</td>
<td>Solid State Relay</td>
<td>Opto 22</td>
<td>G4ODC5</td>
</tr>
<tr>
<td>5</td>
<td>Solid State Relay Control Module</td>
<td>Nu Wave Technologies</td>
<td>SSRMAN-1P-HR</td>
</tr>
<tr>
<td>6</td>
<td>Solid State Relay</td>
<td>Crydom</td>
<td>D2W203F</td>
</tr>
<tr>
<td>7</td>
<td>LabJack U3-LV DB15 connection</td>
<td></td>
<td></td>
</tr>
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<td>8</td>
<td>LabJack U3-LV</td>
<td>LabJack</td>
<td>U3-LV</td>
</tr>
<tr>
<td>9</td>
<td>DB 15 connection inside box</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>DB 15 connection outside box</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Two Position Microelectric Valve Actuator</td>
<td>Vici Valco Instruments Co. Inc.</td>
<td>EDMA</td>
</tr>
<tr>
<td>12</td>
<td>Tenax Thermocouples</td>
<td>Omega</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Multi-position Electric Actuator</td>
<td>Vici Valco Instruments Co. Inc.</td>
<td>E4</td>
</tr>
<tr>
<td>14</td>
<td>PTR-MS external switch port</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>MFC Control Board</td>
<td>Air Quality Design</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>500 sccm Mass Flow Controller</td>
<td>MKS</td>
<td>1179A01352CS1BV</td>
</tr>
<tr>
<td>17</td>
<td>1000 sccm Mass Flow Controller</td>
<td>MKS</td>
<td>1179A01313CS1BV</td>
</tr>
<tr>
<td>18</td>
<td>50 sccm Mass Flow Controller</td>
<td>MKS</td>
<td>1179A01351CS1BV</td>
</tr>
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Table 2.9: VOC and IVOC sensitivities of key species at 80 Td.

<table>
<thead>
<tr>
<th>m/z</th>
<th>compounds</th>
<th>VOC (ncps)</th>
<th>IVOC (AC/nmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>formaldehyde</td>
<td>10.8</td>
<td>5.76E+05</td>
</tr>
<tr>
<td>33</td>
<td>methanol</td>
<td>17.6</td>
<td>9.39E+05</td>
</tr>
<tr>
<td>42</td>
<td>acetonitrile</td>
<td>31.4</td>
<td>1.68E+06</td>
</tr>
<tr>
<td>45</td>
<td>acetaldehyde</td>
<td>32.4</td>
<td>1.73E+06</td>
</tr>
<tr>
<td>59</td>
<td>acetone</td>
<td>27.5</td>
<td>1.47E+06</td>
</tr>
<tr>
<td>69</td>
<td>isoprene</td>
<td>12.2</td>
<td>6.54E+05</td>
</tr>
<tr>
<td>71</td>
<td>methacrolein</td>
<td>11.9</td>
<td>6.38E+05</td>
</tr>
<tr>
<td>73</td>
<td>2-butanone</td>
<td>22.2</td>
<td>1.18E+06</td>
</tr>
<tr>
<td>79</td>
<td>benzene</td>
<td>10.8</td>
<td>5.74E+05</td>
</tr>
<tr>
<td>93</td>
<td>toluene</td>
<td>8.8</td>
<td>4.69E+05</td>
</tr>
<tr>
<td>105</td>
<td>styrene</td>
<td>7.3</td>
<td>3.87E+05</td>
</tr>
<tr>
<td>107</td>
<td>p-xylene</td>
<td>7.0</td>
<td>3.74E+05</td>
</tr>
<tr>
<td>121</td>
<td>1,2,4-trimethylbenzene</td>
<td>5.4</td>
<td>2.88E+05</td>
</tr>
<tr>
<td>135</td>
<td>1,2,3,5-tetramethylbenzene</td>
<td>4.0</td>
<td>2.13E+05</td>
</tr>
<tr>
<td>137</td>
<td>α-pinene</td>
<td>3.8</td>
<td>2.03E+05</td>
</tr>
</tbody>
</table>
Table 2.10: IVOC detection limits of select species during CARES. All detection limits assume an IVOC sample volume of 1 L. The area counts were normalized to MHz H$_3$O$^+$. 

<table>
<thead>
<tr>
<th>Species</th>
<th>m/z</th>
<th>Average Zero (AC)</th>
<th>3σ</th>
<th>IVOC sensitivity (AC/nmol)</th>
<th>Detection Limit (pptv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>93</td>
<td>2342</td>
<td>1695</td>
<td>1.13E+06</td>
<td>1.5</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>121</td>
<td>411</td>
<td>897</td>
<td>6.94E+05</td>
<td>1.3</td>
</tr>
<tr>
<td>1,2,3,5-tetramethylbenzene</td>
<td>135</td>
<td>213</td>
<td>446</td>
<td>5.13E+05</td>
<td>0.9</td>
</tr>
<tr>
<td>alkanes</td>
<td>57, 71, 85, 99</td>
<td>5337</td>
<td>4326</td>
<td>9.88E+04</td>
<td>44</td>
</tr>
<tr>
<td>cycloalkanes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>716</td>
<td>805</td>
<td>1.06E+06</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>468</td>
<td>689</td>
<td>8.39E+05</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>329</td>
<td>652</td>
<td>6.40E+05</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td>136</td>
<td>289</td>
<td>4.66E+05</td>
<td>0.6</td>
</tr>
<tr>
<td>methylnaphthalene</td>
<td>143</td>
<td>1166</td>
<td>3094</td>
<td>4.21E+05</td>
<td>7.4</td>
</tr>
<tr>
<td>C$_2$ naphthenic monoaromatic</td>
<td>161</td>
<td>40</td>
<td>289</td>
<td>2.38E+05</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Table 2.11: Estimated Tenax TA breakthrough volumes of key species. The bold numbers signify breakthrough volumes that are lower than the volume flowed through the Tenax. 86 mL and 125 mL were flowed through the Tenax during the purge and desorption modes respectively.

<table>
<thead>
<tr>
<th></th>
<th>Breakthrough volume (mL) at designated temperature</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Purge Mode</td>
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<tr>
<td>Temperature (°C)</td>
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<tr>
<td>30</td>
<td>125</td>
</tr>
<tr>
<td>Benzene</td>
<td>8330</td>
</tr>
<tr>
<td>Toluene</td>
<td>28350</td>
</tr>
<tr>
<td>p-xylene</td>
<td>107100</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>329350</td>
</tr>
<tr>
<td>p-cymene</td>
<td>741475</td>
</tr>
<tr>
<td>n-octane</td>
<td>41125</td>
</tr>
<tr>
<td>n-nonane</td>
<td>122500</td>
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<tr>
<td>n-decane</td>
<td>308350</td>
</tr>
<tr>
<td>n-undecane</td>
<td>822500</td>
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<tr>
<td>n-dodecane</td>
<td>2975000</td>
</tr>
<tr>
<td>n-tridecane</td>
<td>9616775</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>18212950</td>
</tr>
<tr>
<td>n-pentadecane</td>
<td>36400000</td>
</tr>
<tr>
<td>n-hexadecane</td>
<td>103</td>
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<td>n-heptadecane</td>
<td>156</td>
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<tr>
<td>n-octadecane</td>
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</tr>
<tr>
<td>n-nonadecane</td>
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</tr>
<tr>
<td>n-eicosane</td>
<td></td>
</tr>
<tr>
<td>n-heineicose</td>
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<td>n-docosane</td>
<td></td>
</tr>
<tr>
<td>n-tricosane</td>
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</tr>
<tr>
<td>n-tetracosane</td>
<td></td>
</tr>
<tr>
<td>n-pentacosane</td>
<td></td>
</tr>
<tr>
<td>n-hexacosane</td>
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</tr>
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</table>
Table 2.12: Temperature versus the signal observed during the 30 °C purge temperature from the data in Figure 2.24. The bolded percentages signify species with greater than 90% removal.

<table>
<thead>
<tr>
<th>Group</th>
<th>m/z</th>
<th>Diesel</th>
<th>Gasoline</th>
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<tr>
<td>cycloalkanes</td>
<td>83</td>
<td>95%</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td>97</td>
<td>89%</td>
<td>98%</td>
</tr>
<tr>
<td></td>
<td>111</td>
<td>82%</td>
<td>94%</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>74%</td>
<td>92%</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td>71%</td>
<td>93%</td>
</tr>
<tr>
<td>bicycloalkanes</td>
<td>123</td>
<td>62%</td>
<td>78%</td>
</tr>
<tr>
<td></td>
<td>137</td>
<td>52%</td>
<td>69%</td>
</tr>
<tr>
<td></td>
<td>151</td>
<td>61%</td>
<td>70%</td>
</tr>
<tr>
<td></td>
<td>165</td>
<td>66%</td>
<td>86%</td>
</tr>
<tr>
<td></td>
<td>179</td>
<td>64%</td>
<td>92%</td>
</tr>
<tr>
<td>alkylbenzenes</td>
<td>79</td>
<td>93%</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td>93</td>
<td>91%</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>107</td>
<td>63%</td>
<td>97%</td>
</tr>
<tr>
<td></td>
<td>121</td>
<td>36%</td>
<td>90%</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>21%</td>
<td>75%</td>
</tr>
<tr>
<td></td>
<td>149</td>
<td>29%</td>
<td>60%</td>
</tr>
<tr>
<td></td>
<td>163</td>
<td>29%</td>
<td>55%</td>
</tr>
<tr>
<td>naphthenic monoaromatics</td>
<td>119</td>
<td>58%</td>
<td>88%</td>
</tr>
<tr>
<td></td>
<td>133</td>
<td>28%</td>
<td>72%</td>
</tr>
<tr>
<td></td>
<td>147</td>
<td>16%</td>
<td>61%</td>
</tr>
<tr>
<td></td>
<td>161</td>
<td>39%</td>
<td>58%</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>27%</td>
<td>61%</td>
</tr>
<tr>
<td>naphthalenes</td>
<td>129</td>
<td>39%</td>
<td>56%</td>
</tr>
<tr>
<td></td>
<td>143</td>
<td>25%</td>
<td>41%</td>
</tr>
<tr>
<td></td>
<td>157</td>
<td>21%</td>
<td>39%</td>
</tr>
<tr>
<td>Alkanes and alkenes</td>
<td>57, 71, 85, 99, 113</td>
<td>93%</td>
<td>97%</td>
</tr>
</tbody>
</table>
Figure 2.1: Proton affinities for selected compounds found in urban air. Anything with a proton affinity greater than water is detectable by the PTR-MS.
Figure 2.2: Schematic of PTR-MS ion source and drift tube.
Figure 2.3: Schematic of PTR-MS Sample Inlet
Figure 2.4: PTR-MS bar scan at 80 Td taken during the CARES campaign. Signal is shown in counts per second (Hz)
Figure 2.5: PTR-MS bar scans at 120 Td for dry nitrogen from a liquid nitrogen dewer (top panel) and zero air generated from a Pt catalyst (bottom panel).
Figure 2.6: PTR-MS ion transmission curve observed in laboratory.
Figure 2.7: PTR-MS mass spectrum of gasoline exhaust (top) and diesel exhaust (bottom) at 80 Td. Ion signal has been color coded to assign ions to common fragmentation patterns that identify common organic compound classes: alkane fragment ions (black), alkylbenzenes (blue), cycloalkane fragment ions (green) and naphthenic monoaromatics (red).
Figure 2.8: Plumbing schematic showing thermal desorption sampler for IVOC compounds and VOC sampling system with water vapor trap.
Figure 2.9: Plumbing diagram illustrating gas flows for the 4 different modes of IVOC operation. Red lines indicate flow path through the Tenax trap. Black lines indicate other gas lines. Numbers refer to components described in Table 2.5.
Figure 2.10: Schematic of the electronics within the IVOC sampler. Numbers refer to parts listed in Table 2.6.
Figure 2.11: Schematic of the DaqFactory wiring configuration of the IVOC sampler. The numbers correspond to parts listed in Table 2.8. The color of the wires matches those used, except the brown represents the use of a white wire.
Figure 2.12: Screenshot of the IVOC sampler automation.
Figure 2.13: Screenshot of the IVOC sampler data processing.
Figure 2.14: Typical thermal desorption profile for 1,3,5-trimethylbenzene (m/z 121) shown in grey and corresponding zero shown as blue shading. Bottom panel shows corresponding Tenax trap temperature. The signal (Hz) shown is normalized by MHz H$_3$O$^+$. 
Figure 2.15: Determination of the desorption peak base width for 1,2,3,5-tetramethylbenzene ($m/z$ 135). The start of the base width (1st red line) is determined when the signal (green) is higher than one standard deviation (blue) above the average background ion signal (black). The end of the base width (2nd red line) is determined when the signal drops back down below the blue trace. The ion signal (Hz) shown is normalized to MHz $\text{H}_3\text{O}^+$. 
Figure 2.16: Upper panel shows a time series of the 1,3,5-trimethylbenzene ion signal ($m/z$ 121) from a prepared test mixture as measured in VOC mode passing through the water trap (blue shading) and from desorption of a 257 cc air sample of the test mixture collected on the Tenax trap (red shading). The bottom panel shows the gas flow through the Tenax trap. The shaded area A1 in VOC mode corresponds to the IVOC sample collection time.
Figure 2.17: Average zeros and associated error observed during the CARES and Lovelace studies. The signals (Hz) were normalized to MHz H$_3$O$^+$. 
Figure 2.18: Average zeros observed during desorption after varying purge temperatures. Most of the observed ions had similar zeros under all purge temperatures (bottom panel). For a few ions (m/z 57, 83, 85, 87, 93, 101, 105) there seemed to be a dependence on purge temperature, with lower purge temperatures leading to higher zero averages (top panel).
Figure 2.19: PTR-MS IVOC mode desorption peaks of selected compounds for 30 °C (blue trace) and 150 °C purge (red trace) temperatures: methacrolein (m/z 71), benzene (m/z 79), toluene (m/z 93), p-xylene (m/z 107), 1,2,4-trimethylbenzene (m/z 121), 1,2,3,5-tetramethylbenzene (m/z 135), decane (m/z 57, 71, 85, 99), dodecane (m/z 57, 71, 85, 99), and pentadecane (m/z 57, 71, 85, 99). The ion signal (Hz) is normalized to MHz \( \text{H}_2\text{O}^+ \).
Figure 2.20: Removal rate of n-alkanes (top panel) and alkylbenzenes (bottom panel) observed during the 150 °C purge scenario. In the gas standard the alkylbenzene compounds correspond to benzene (m/z 79), toluene (m/z 93), p-xylene (m/z 107), 1,2,4-trimethylbenzene (m/z 121) and
1,2,3,5-tetramethylbenzene ($m/z$ 135).

Figure 2.21: Mixing ratios of select species observed in gasoline and diesel exhaust during the Lovelace chamber study. Both engines were under a typical load, with the diesel exhaust being diluted by ~25% and the gasoline being diluted by ~60%.
CHAPTER 3: MEASURING LONG CHAIN ALKANES IN DIESEL EXHAUST BY THERMAL DESORPTION PTR-MS

3.1. Abstract

A method using thermal desorption sampling and analysis by PTR-MS to measure long chain alkanes (C_{12}-C_{18}) and other larger organics associated with diesel engine exhaust emissions is described. Long chain alkanes undergo dissociative proton transfer reactions forming a series of fragment ions with formula C_{n}H_{2n+1}. The PTR-MS is insensitive to n-alkanes less than C_{8} but displays an increasing sensitivity for larger alkanes. Fragment ion distribution and sensitivity is a function of drift conditions. At 80 Td the most abundant ion fragments from C_{10} to C_{16} n-alkanes were m/z 57, 71 and 85. The mass spectrum of gasoline and diesel fuel at 80 Td displayed ion group patterns that can be related to known fuel constituents, such as alkanes, alkylbenzenes and cycloalkanes, and other compound groups that are inferred from molecular weight distributions such as dihydronapthalenes and naphthenic monoaromatics. It is shown that thermal desorption sampling of gasoline and diesel engine exhausts at 80 Td allows for discrimination against light alkanes and alkenes which are a major constituent of both exhausts, allowing for quantification of higher molecular weight alkanes from the abundance of C_{n}H_{2n+1} fragment ions. Using this approach, the molar abundance of C_{12}-C_{18} alkanes in diesel engine exhaust was found to be 75% that of the total C_{1}-C_{4} alkylbenzene abundance. While the PTR-MS mass spectra of gasoline and diesel exhaust looked similar, the abundance of higher molecular weight compounds relative to that of C_{4}-alkylbenzenes was much greater in diesel engine exhaust. The abundance patterns of compounds determined by thermal desorption sampling may allow for emission profiles to be developed to better quantify the relative contributions of diesel and gasoline exhaust emissions of larger organic compounds to urban air concentrations.
3.2. Experimental

3.2.1. Thermal Desorption Sampler

A general description of the IVOC sampler is located in Section 2.2.

3.2.2. Dynamic Dilution System

The dynamic dilution system was utilized for calibrating low vapor pressure species within the PTR-MS and is detailed in Section 2.3.4.

3.2.3. Engine Exhaust Sampling

Diesel and gasoline engine exhaust were sampled from inhalation exposure chambers at the Lovelace Respiratory Research Institute in Albuquerque, NM. The diesel engine was a 5.5 kW Yanmar diesel electric generator and the gasoline engine a 1996 model General Motors 4.3-L V-6 mounted to a dynamometer. The emissions from these engines and facility description are described in more detail in McDonald et al. (2004; 2007; 2011). The facility can blend diesel and gasoline engine exhaust in different proportions and thus provided an excellent opportunity to test the IVOC thermal desorption sampler. Over a series of tests, the engine load was varied and the exhaust diluted to different extents with clean, dry air. A portion of the diluted exhaust flow was diverted through a 1.5 m$^3$ exposure chamber from which the PTR-MS sampled. The inlet for the PTR-MS consisted of a heat traced electropolished steel tubing (UHP Cardinal) protected by a 1.0 µm Teflon particle filter that was replaced after each experiment.

3.3. Results

3.3.1. n-Alkane Response

As detailed in section 2.1.1, the PTR-MS instrument measures organics (R) via a proton transfer reaction with H$_3$O$^+$ producing a mass spectrum of an air sample that is ideally interpreted as an molecular weight +1 (M+1) mass spectrum.
\[
H_3O^+ + R \rightarrow H_2O + RH^+ \quad (R1)
\]

However, many dissociative proton transfer reactions are known to occur complicating this interpretation. Reaction R1 will be exothermic if the species R has a higher proton affinity (PA) than H_2O and exothermic proton transfer reactions occur near their collision rate limit (Bohme et al., 1979), making the PTR-MS sensitive to a wide variety of organic compounds. The proton affinity of H_2O is 166.5 ± 2 kcal mol\(^{-1}\) at 298 K (Lias et al., 1984) and the proton affinities for larger alkanes approach this value (Hunter and East, 2002). Spanel and Smith (1998) measured H_3O^+ reactions with alkanes using a selected ion flow tube. It was found that larger n-alkanes can form an adduct with the hydronium ion:

\[
H_3O^+ + C_{10}H_{22} + M \rightarrow H^+(H_2O)C_{10}H_{22} + M \quad (R2)
\]

The study also observed a ligand switching reaction that occurs in the presence of water vapor that catalyzed the formation of water clusters:

\[
H^+(H_2O)C_{10}H_{22} + H_2O \rightarrow H^+(H_2O)_2 + C_{10}H_{22} \quad (R3)
\]

In our studies with the PTR-MS instrument, adducts were observed during measurement of the n-alkanes at 80 Td but at very low abundance. There was also an increase in the \(m/z\) 37 ion abundance due to the water cluster \(H^+(H_2O)_2\) perhaps a result of reaction R3. In the PTR-MS there are also reactions that occur with O_2^+ ions created in the ion source that confound the interpretation of the PTR-MS mass spectrum as a simple M+1 mass spectrum. O_2^+ reacts rapidly with alkanes causing extensive fragmentation (Spanel and Smith, 1998). To minimize the influence of O_2^+, dry N_2 was used as the diluent gas in the dynamic dilution system and in thermal desorption from the adsorbent trap. Typically O_2^+ ion count rates were less than 0.1% of the \(H_3O^+\) count rate.
The PTR-MS response to n-alkanes was determined for 120 Td and 80 Td drift tube conditions by preparing known mixtures with the dynamic dilution system. The n-alkanes undergo dissociative proton transfer reactions in the PTR-MS (Jobson et al., 2005) producing fragmentation patterns similar to electron impact ionization. Figure 3.1 shows the fragmentation pattern for dodecane as an example of the typical pattern observed for n-alkanes. The C₈-C₁₆ n-alkanes produce a significant response and their spectra displayed similar features, yielding a pattern of fragment ions with the formula CₙH₂ₙ₊₁ for n ≥ 3. For heptane and smaller n-alkanes there was little response and these species appear to be unreactive with H₃O⁺ at these drift tube conditions. The n-alkane fragmentation pattern was a function of the Townsend number. At lower Townsend numbers there was less fragmentation into lighter ions. At 80 Td there was essentially no fragmentation to m/z 41 and 43 while at 120 Td these were two of the most abundant fragment ions.

The benefit of operating at lower Td is that the n-alkane ion signal occurs at larger ion masses allowing for better distinction between IVOC and VOC species. The ions m/z 41, 43 and 57 are common fragment ions from a wide range of species and are typically the most abundant ion signals in PTR-MS analysis of urban air. At 80 Td, approximately 70% of the ion signal occurs at m/z 57, 71, and 85 for the C₉ to C₁₆ n-alkanes. There would be significant interference from VOC compounds found in urban air for m/z 57 (from butenes) and m/z 71 (from pentenes, methacrolien, methyl vinyl ketone). To use these ions to monitor for IVOC alkanes will require a discrimination strategy to prevent interfering VOCs from being measured during thermal desorption. Our approach, described in more detail below, is to purge the Tenax trap at an elevated temperature after sample collection to remove these VOCs, then desorb the trap at higher temperatures to measure the heavier organics that remain. The ions m/z 85, 99, 113, and
127 may be more unique tracers of long chain alkane abundance in the atmosphere. Preliminary tests have shown that branched and iso-alkanes display similar fragmentation patterns and sensitivity as n-alkanes except there is a more significant M-1 peak for iso-alkanes, typically on the order of 10% of the total fragment ion signal.

The PTR-MS instrument’s sensitivity to alkanes was determined by preparing known n-alkane and toluene mixtures using the dynamic dilution system. The sum of the normalized response at all ions was divided by the mixing ratio to get sensitivity in units of Hz ppbv$^{-1}$ per MHz H$_3$O$^+$ (ncps). The alkane species of interest was co-injected with toluene to ensure the syringe pump was operating correctly, since an expected signal for toluene can be calculated from a known response to external gas phase standards. The n-alkane sensitivity is shown in Figure 3.2. The response curve displays a dependence on the drift conditions. The PTR-MS is insensitive to alkanes with carbon numbers $< C_8$. The increase in sensitivity for alkanes $> C_7$ is consistent with the rate constant measurements of Arnold et al. (1998) which are also shown in the figure. Quantum mechanical calculations of alkane C-C bond proton affinities reveal that the more central bonds of the molecule have the largest proton affinities and for larger alkanes approach that of water at 166.5 kcal/mole (Hunter and East, 2002). The H$_3$O$^+$ + n-alkane reaction appears to be endothermic and explains why the n-alkane sensitivity is significantly lower than that of toluene. Using the summed ion signal for all C$_n$H$_{2n+1}$ (n$\geq$3) fragment ions, the normalized sensitivity for dodecane at 120 Td was 2.4 ncps compared to 9 ncps for toluene. The PA of n-alkanes appears to plateau for larger alkanes and the 120 Td sensitivity curve suggests a sensitivity plateau as well for n-alkanes $> C_{14}$. At the 80 Td condition normalized sensitivities should increase due to the 150% increase in reaction time. The expected sensitivity increase was observed for toluene but not the n-alkanes. The similarity in sensitivity for C$_8$-C$_{11}$ n-alkanes at
the two drift conditions may be due to the decrease in reaction rate at lower ion energies at 80 Td offsetting the increase in reaction time. At 120 Td the n-alkane sensitivity is primarily determined by the ion signal at $m/z$ 41, 43 and 57 while at 80 Td the sensitivity is determined by a broader range of heavier ion masses, as illustrated in Figure 3.1, with most of the ion signal (>50%) at $m/z$ 57, 71, 85.

3.3.2. Diesel and Gasoline Fuel Mass Spectra

To better understand what constituents of vehicle fuels and exhausts the PTR-MS may respond to, gasoline and diesel fuel #2 used in the engine exhaust studies were measured by evaporating 5 µL hr$^{-1}$ of whole fuel into 20 slpm of dry nitrogen in the dynamic dilution system at 60 °C. The PTR-MS sampled directly from this flow, by-passing the thermal desorption sampler and water trap. Gasoline is mostly comprised of hydrocarbons in the C$_4$ to C$_{10}$ range compared to the C$_8$ to C$_{25}$ range for diesel fuel (Han et al., 2008; Schauer et al., 1999; Lough et al., 2005; Gentner et al., 2012; Wang et al. 2005). Distinct ion groups were observed in both fuel types that can be related to different organic compound classes. Exhausts are a more complex mixture that will contain these fuel species plus oxygenated species such as aldehydes and furans, and other hydrocarbons such as alkenes, acetylene, and pyrogenic compounds (Schauer et al., 1999; Schauer et al., 2002). Both fuels were sampled at 80 and 120 Td drift conditions and the resulting mass spectra are shown in Figure 3.3. The gasoline contained 10% ethanol by volume and ethanol appears at $m/z$ 47 and an ethanol water cluster ion at $m/z$ 65 in the gasoline mass spectra. The relative intensity of the peaks gives a qualitative indication of the relative molar abundance of the different constituents; the ion intensities were not corrected for differences in ion transmission efficiency and compound sensitivity. The PTR-MS mass spectrum for gasoline ends around $m/z$ 180 while significant ion signal in the diesel fuel mass
spectrum was still observed to $m/z$ 240. There are more pronounced differences in the 120 Td and 80 Td mass spectra of diesel fuel than gasoline, with significant shifts to higher $m/z$ ions for the $C_nH_{2n+1}$ and $C_nH_{2n-1}$ ion groups in diesel fuel, suggesting significant fragmentation of hydrocarbons.

Comprehensive analysis of diesel fuel has shown that approximately 70% by mass is composed of saturated compounds, of which 30% are n-alkanes and branched alkanes, and 21% cycloalkanes, and 18% of the fuel by mass is monoaromatic compounds, with no contribution from alkenes (Venduevre et. al., 2005; Gentner et al., 2012). The series of ions in diesel fuel corresponding to masses $C_nH_{2n+1}$ for $n \geq 3$, as listed in Table 3.1, are attributed to alkanes and these masses are shown as black bars in Fig. 3.4. Significant differences in the relative ion intensity for the alkane fragment ions are observed between the 120 and 80 Td conditions. Alkanes are also a significant component of gasoline but the PTR-MS is relatively insensitive to alkanes with less than 8 carbons. For summer blends of gasoline, alkanes with 8 or more carbon atoms comprise about 30% of the total alkane composition on a molar basis (Lough et al., 2005; Gentner et al., 2012) and these compounds would produce a signal at the $C_nH_{2n+1}$ ion masses. Contributions to signal at $m/z$ 57, 71, and 85 could also be due to $C_4$-$C_6$ alkenes. These species comprise a much smaller molar fraction of whole gasoline, on the order of 4% (Lough et al., 2005; Gentner et al., 2012) but the PTR-MS is much more sensitive to these species than alkanes. Given the negligible response of the PTR-MS to $C_4$-$C_7$ alkanes, and the low molar abundance of $C_3$-$C_6$ alkenes and alkanes > $C_8$ in gasoline, the gasoline PTR-MS mass spectrum of gasoline is thus dominated by the alkylbenzene constituents, in particular toluene ($m/z$ 93) and the xylene isomers ($m/z$ 107).
The prominent group of ions with mass formula \( \text{C}_n\text{H}_{2n-1} \) \( (n \geq n) \) was attributed to alkyl substituted cycloalkanes as listed in Table 3.1 and indicated as green bars in Fig. 3.4. Gentner et al. (2012) have reported the presence of \( \text{C}_7 \) to \( \text{C}_{25} \) cycloalkane compounds in diesel fuel, with mass fractional contribution by carbon number ranging from 0.15% for \( \text{C}_7 \) compounds to 2.2% for \( \text{C}_{10}, \text{C}_{11}, \) and \( \text{C}_{12} \) compounds, diminishing to 1.1% for \( \text{C}_{18} \) compounds, the apparent upper limit of our experimentally observable range. As noted in Table 3.1, this ion group comprised 17.7% of the total ion signal for diesel fuel at 80 Td and 5.4% for gasoline, with ions \( m/z \) 69, 83, 97, 111 and 125 the most abundant. Laboratory tests confirmed that cycloalkanes yield these ions at 80 and 120 Td drift tube conditions. At 80 Td these compounds yielded an \( \text{M}-1 \) ion as the major fragment ion. For example, methylcyclohexane and 1,2-dimethylcyclohexane yielded \( \text{M}-1 \) ions at \( m/z \) 97 and \( m/z \) 111 respectively with greater than 85% total ion abundance.

Cyclohexane also yielded a strong \( \text{M}-1 \) ion signal at \( m/z \) 83, but a more intense \( \text{M}+1 \) ion at \( m/z \) 85. The compound 1,3,5-trimethylcyclohexane produces an \( \text{M}-1 \) ion at 80 Td but fragments at 120 Td to yield \( m/z \) 69 as the most abundant ion. Cyclohexane has a proton affinity less than that of \( \text{H}_2\text{O} \) and our tests suggest the PTR-MS is more sensitive to alkyl substituted cyclohexanes, implying they have greater proton affinity. For diesel fuel at 80 Td, the ion signal for this group was more intense than the corresponding alkane ion at a similar mass. The ion intensity for this group was relatively uniform from \( m/z \) 97 to \( m/z \) 153, and then decreased rapidly to the heaviest ion measured at \( m/z \) 237, corresponding to a \( \text{C}_{17} \) compound.

The alkylbenzene compounds identified as blue bars in Figure 3.3 and listed in Table 3.1 are also prominent in diesel fuel mass spectra, comprising 20% of the total ion signal at 80 Td. Ion signal for these species ranges from \( m/z \) 79 (benzene) to \( m/z \) 233 indicating a \( \text{C}_{18} \) alkylbenzene. Most of the ion intensity was at \( m/z \) 121 and 135 corresponding to alkylbenzene
compounds with 9 and 10 carbon atoms respectively; these are identified as C$_3$-alkylbenzenes and C$_4$-alkylbenzenes to indicate the number of carbon atoms in the alkyl groups attached to the benzene ring. The Gentner et al. (2012) analysis of diesel fuel reports the most abundant aromatics by carbon number are C$_{10}$ compounds at 2.4% by weight carbon, decreasing gradually to 0.8% abundance for C$_{18}$ compounds, the limit of our observable range, down to 0.2% for C$_{25}$ compounds. Examination of the alkylbenzene ion abundance relative to m/z 149 showed that fragmentation of higher molecular weight aromatics was occurring as evidenced by much larger abundance of m/z 79, 93, and 107 ions at 120 Td than at 80 Td. At 120 Td m/z 79 was a factor of 7 more abundant, m/z 93 was 3 times more abundant, and m/z 107 was 1.4 times more abundant. The relative abundance of m/z 135 and ions larger than m/z 149 were very similar for the two drift conditions, within 5%, with the exception of m/z 233 which was a factor of 2 higher at 80 Td. Tests performed on fragmentation patterns for a suite of methyl, ethyl, n-propyl, i-propyl, and n-pentyl alkyl substituted benzene compounds have shown that few compounds fragment at the 80 Td drift field energies, exceptions being compounds with isopropyl groups. For example, 10% of p-cymene fragments to produce at ion at m/z 93. At 120 Td a greater degree of fragmentation was observed and m/z 79 and m/z 93 were common fragment ions. The occurrence of an ion at m/z 79 (benzene) in diesel fuel may be entirely due to fragmentation of larger alkylbenzene compounds. It was also observed that some aromatic compounds (i.e. n-pentylbenzene, 1,3-diisopropylbenzene, 2,2-dimethyl-1-propylbenzene) yielded significant fragmentation to m/z 43. Operating the PTR-MS at lower Td values will provide a higher fidelity measure of alkybenzene mass distribution in diesel fuel given the prevalence of higher molecular weight alkybenzene compounds. The alkybenzene compounds are isobaric with the tricycloalkanes compounds identified in diesel fuel by Gentner et al. (2012). The abundance of
tricycloalkanes to alkylbenzene compounds range from a factor of 0.05 for C\textsubscript{10} tricycloalkanes to a factor of 0.5 for C\textsubscript{18} tricycloalkanes.

An ion group with a formula C\textsubscript{n+9}H\textsubscript{2n+11} (n≥0) makes up 14% of total diesel fuel ion signal at 80 Td but less than 2% of the gasoline mass spectra as shown as red bars in Figure 3.3 and listed in Table 3.1. If the ion signal pattern can be interpreted as an M+1 mass spectrum then this group could be a series of alkyl substituted indane (C\textsubscript{9}H\textsubscript{10}) and 1,2,3,4-tetrahydronaphthalene (tetralin, C\textsubscript{10}H\textsubscript{12}) compounds. Laboratory tests demonstrated that at 80 Td indane and tetralin yield M+1 ions at m/z 119 and 133 respectively, with no fragmentation. Such compounds are comprised of a benzene ring fused to a cycloalkane structure. The presence of such naphthenic monoaromatics has been reported in diesel fuel (Vendeuvre et al., 2005; Vendeuvre et al., 2007). Ions at m/z 91 and 105 may also belong to this series, possessing a 3 or 4 member alkyl ring structure respectively. The ring structure is isobaric with an alkene functional group but there are few reports of alkenes being prominent in diesel fuel.

About 8% of the diesel fuel mass spectrum is comprised of an ion group with mass formula C\textsubscript{n+5}H\textsubscript{2n+7} (n≥0). This group contributes less than 1% of the ion signal in the gasoline mass spectrum. These compounds may be bicycloalkanes (C\textsubscript{8}H\textsubscript{14}, C\textsubscript{9}H\textsubscript{16}, C\textsubscript{10}H\textsubscript{18}) and related alkyl substituted compounds. Bicycloalkanes with 10 or more carbon atoms have been identified as a significant constituent in diesel fuel (Gentner et al., 2012). Laboratory experiments at 80 Td demonstrated that decahydronaphthalene (C\textsubscript{10}H\textsubscript{18}) yields an M-1 ion at m/z 137 with no fragmentation. At 120 Td there was significant fragmentation to m/z 67, 81 and 95 accounting for 1, 50, and 11% of the signal respectively with 38% of the response at m/z 137. Naphthalene and alkylsubstituted naphthalenes with mass formula C\textsubscript{n+10}H\textsubscript{2n+9} (n≥0) and dihydronaphthalenes, C\textsubscript{n+10}H\textsubscript{2n+11}, both yield M+1 ions at 80 Td as demonstrated in laboratory tests. These compounds
comprise a small fraction of the fuel ion signal. Their masses and total group ion signal abundance are listed in Table 3.1.

The relative contributions from each of these compound classes can be illustrated in Figure 3.4 which shows the PTR-MS mass spectrum for diesel fuel measured at 80 Td over the C\textsubscript{12} to C\textsubscript{14} carbon number range. Sensitivities for unsaturated compounds will likely be similar and thus the relative ion abundance reflects relative molar composition for a particular carbon number. The figure shows a similar pattern of group abundance for the different carbon number ranges, arranged by mass from the least saturated compounds (naphthalenes) to the most saturated compounds (alkanes). The identifications are tentative and need to be verified by more specific analytical techniques, but suggest that soft ionization by H\textsubscript{3}O\textsuperscript{+} may be useful for characterizing the compound group composition of diesel fuel. In this analysis the naphthenic monoaromatics, possibly alkylsubstituted tetralin compounds, are more abundant than the equivalent carbon number alkylbenzenes in the C\textsubscript{12} to C\textsubscript{14} range.

3.3.3. Diesel and Gasoline Exhaust Mass Spectra

Representative mass spectra of diesel and gasoline engine exhaust are shown in Figure 3.5. Ions are grouped and color coded by compound classes as was done for the fuel. The data were collected at 80 Td in VOC mode using a -30 °C dehumidifier to remove water vapor and to some extent, depending on exhaust concentrations, lower volatility organics. Shown are ions measured in selective ion measuring mode of the PTR-MS and include major ions from the compound groups identified in diesel fuel plus ions attributed to oxygenated species known to be emitted in exhaust such as formaldehyde (m/z 31), acetaldehyde (m/z 45) and acetone + propanal (m/z 59). The diesel engine was operated under a low engine load, the gasoline engine was under a typical engine load and both exhausts were diluted with similar flows of dry air. For a
similar level of dilution, gasoline exhaust displayed much higher concentrations of VOCs. For both engine types the major organic compounds in exhaust have been reported to be aldehydes, light alkenes and alkanes, and alkylbenzenes (Hoekman, 1992; Schauer et al., 1999, Schauer et al., 2002; Schmitz et al., 2000; Smith et al., 2002; Jobson et al., 2005). The exhaust composition is thus significantly different than the fuel composition, particularly for diesel exhaust, where a large fraction of the mass emission rate is comprised of low molecular weight compounds not present in the fuel. This compositional change is reflected in the PTR-MS mass spectrum with prominent peaks associated with aldehydes and ketones (m/z 31, 45, 59, 73), light alkenes (m/z 43, 57, 71), and alkylbenzenes (m/z 79, 93, 107, 121, 135). The PTR-MS mass spectrums of the diesel and gasoline engine exhaust thus appear quite similar. Table 3.2 compares the percentage of ion signal found for selected ions within the different compound groups for the fuel and exhaust. For PTR-MS measurements of long chain alkanes and other IVOC species associated with engine exhaust in urban air, it will be necessary to both discriminate against the very abundant light alkenes which produce interfering ions for the measurement of IVOC alkanes and to preconcentrate the air sample to improve detection of the much lower abundant IVOC range species. For example, the ion signal for IVOC alkylbenzenes with carbon numbers of 10 or greater is about 2 orders of magnitude less than xylenes at m/z 107. This need motivates thermal desorption sampling that can both discriminate against volatile alkenes and preconcentrate IVOC compounds.

3.3.4. Thermal Desorption Sampling

A description of the thermal desorption sampling can be found in Section 2.3.2 and the calculation of IVOC sensitivities can be found in Section 2.3.3.
3.3.5. VOC Discrimination

By purging the Tenax trap before desorption, the light alkenes and other VOCs can be removed to make identification of IVOC alkanes and other species tractable. Several desorption purge temperatures were tested to find the optimum temperature for VOC discrimination without significant loss of IVOC alkane species. A 150 °C purge temperature was chosen as this provided effective removal of interfering VOC compounds while limiting losses of C\textsubscript{12} and larger alkanes. In section 2.3.7.2, Figure 2.19 showed an example of the effectiveness of the trap purge for several species. Methacrolein, benzene, toluene, p-xylene, 1,2,4-trimethylbenzene, 1,2,3,5-tetramethylbenzene, decane, dodecane, and pentadecane were sampled onto the trap and subjected to two purge temperatures of 30 °C and 150 °C. Given the breakthrough volumes for these compounds, no loss would be expected for the 30 °C purge and this temperature was used as a reference to compare to other desorption temperatures. Methacrolein, benzene and toluene were removed by the 150 °C purge flow with 98±7%, 99±5% and 97±5% reduction in their respective peak areas. The purge flow at 150 °C effectively removed alkanes and alkenes < C\textsubscript{9} and n-aldehydes < C\textsubscript{7}. Decane, dodecane, and pentadecane peak areas were reduced by 84%, 52%, and 7.5% respectively. The noticeable offset of the pentadecane desorption peaks in Figure 2.19 is due to the migration of pentadecane further along the Tenax adsorbent bed with the 150 °C purge flow. The IVOC thermal desorption sampler thus measures alkanes from the C\textsubscript{12}-C\textsubscript{18} range with the upper range limited by the ability to effectively transfer low volatility compounds through PTR-MS sample lines and valves.

Given the complexity of alkane composition in diesel fuel and exhaust, whole diesel fuel might be a better standard to calibrate PTR-MS sensitivity to the alkane species of interest. Given the mass composition of C\textsubscript{8}-C\textsubscript{18} alkanes in diesel fuel reported by Gentner et al. (2012), a
sensitivity of 2.6 Hz ppbv$^{-1}$ per MHz H$_3$O$^+$ was determined from the sum of the C$_n$H$_{2n+1}$ ions observed from diesel fuel measured by the IVOC sampler under the 150 °C purge condition. This value accounts for losses of alkanes in the purge and represents the average PTR-MS sensitivity to these compounds at 80 Td. This value is larger than n-alkane sensitivities shown in Figure 3.2, and requires further investigation of branched alkane sensitivities and total molar abundance of alkanes in diesel fuel to reconcile this difference. Our method sensitivity is 1.5 Hz ppbv$^{-1}$ per MHz H$_3$O$^+$. This value does not account for losses of longer chain alkanes in the purge. The 1.5 Hz ppbv$^{-1}$ per MHz H$_3$O$^+$ sensitivity factor was used to estimate IVOC alkane abundance in exhaust.

Figure 3.6 illustrates the discrimination against light alkenes in engine exhaust by the thermal desorption sampler. Shown in the figure is a time series of the C$_n$H$_{2n+1}$ ion group response associated with alkenes and larger alkanes present in diesel and gasoline engine exhaust. The exhausts were analyzed by alternating between VOC mode sampling using a -30 °C dehumidifier and IVOC mode sampling using 150 °C purge to remove volatile compounds. The IVOC sample size was 135 mL. The same suite of ions was measured in both modes with dwell times for m/z 43, 57, 71, 85, and 99 of 50 ms and dwell times for m/z 113 and 127 of 100 ms. The exhausts were diluted by a similar amount so the ion signals reflect differences in absolute organic compound emission rates from these engines. Much higher VOC mode responses were observed in gasoline exhaust for the lighter ions m/z 43, 57, 71, 85, attributed to emissions of propene, butenes, pentenes, and hexenes respectively. In IVOC mode the signal for these ions is greatly diminished because these volatile compounds are effectively purged from the trap before desorption into the PTR-MS drift tube. The small remaining signal was attributed to the IVOC alkanes. The IVOC mode ion signal for the larger alkane ions m/z 99, 113, 127 was
more prominent relative to the VOC mode signal. The \( m/z \) 127 ion displayed a greater response in diesel exhaust, consistent with larger mass emissions of \( > \text{C}_{12} \) alkanes in diesel exhaust than gasoline exhaust (Schauer et al., 1999; Schauer et al., 2002). Alkanes and alkenes are major constituents of engine exhausts making up about 60% of gasoline exhaust (Schauer et al., 2002) and 12% of the diesel exhaust non-methane organic gas mass emission rate (Schauer et al., 1999). The PTR-MS is insensitive to alkanes \( \text{C}_7 \) or smaller in size, which make up approximately 18% of the gasoline exhaust emissions and 2% of the diesel exhaust. Additionally, the IVOC sampling mode discriminates against alkanes and alkenes \( < \text{C}_9 \). It is thus estimated that only 1% of the total alkane and alkene emissions from gasoline engine exhaust is measurable by IVOC mode sampling. For diesel engine exhaust, IVOC mode sampling measures approximately 26% of the total alkane and alkene emission rate.

3.3.6. Vehicle Exhaust IVOC Mixing Ratios and Source Fingerprint

Sensitivities were applied to convert VOC and IVOC mode data from diesel exhaust sampling at 80 Td into molar mixing ratios (ppbv). Sensitivities were determined from calibrations from a gas standard or dynamic dilution experiments. For compounds that were not readily available, the sensitivity was estimated from compounds with a known response and similar mass by accounting for differences in the calculated collisional rate constants (Su, 1988). Mixing ratios of selected species in diluted diesel exhaust are shown as a bargraph in Figure 3.7 to illustrate relative molar abundance of the largest ions signals from the compound groups listed in Table 3.2. It was assumed that the \( m/z \) 43, 57, 71 and 85 ions measured in VOC mode represent the corresponding \( \text{C}_3, \text{C}_4, \text{C}_5, \text{C}_6 \) alkenes, although these are common fragment ions. IVOC alkanes are represented as a separate bar. The oxygenated compounds formaldehyde \( (m/z \) 31), acetaldehyde \( (m/z \) 45), and acetone + propanal \( (m/z \) 59), the light alkenes, and the
alkylbenzenes are the most abundant families in the VOC mode. The most abundant species in diesel exhaust are reported to be formaldehyde and acetaldehyde (Schauer et al, 1999). In Figure 3.7, the most abundant compounds are propene (m/z 43) and butenes (m/z 57), ions whose abundance may be enhanced due to fragmentation from other compounds.

The mixing ratio pattern observed in the IVOC mode in Figure 3.7 illustrates discrimination against the volatile species (oxygenates, alkenes, cycloalkanes) and comparable mixing ratios to those measured in VOC mode for high molecular weight compounds. The light alkylbenzenes (m/z 79, 93) are essentially removed with the 150 °C purge, so the limited response was attributed to fragmentation of larger alkylbenzenes. The difference between VOC and IVOC mixing ratios at m/z 79, 93, 107, and 121 are 97, 95, 80, and 63% respectively which are similar to the corresponding removal rates observed in Figure 2.19 of 99, 97, 86, and 65%. The heavy alkylbenzene (m/z 149, 163) mixing ratios were similar in both the VOC and IVOC modes as be expected for lower volatility species that aren’t removed by the Tenax trap purge. Good agreement was also observed for the bicycloalkane responses at m/z 123 and 137 and the naphthenic monoaromatic responses at m/z 133 and 147, with the IVOC mixing ratios being within 15% of the VOC missing ratios. Improvements in detection from the IVOC sampler were observed at the naphthenic monoaromatic ion m/z 175 and the naphthalene ion m/z 157, with the IVOC mixing ratio being larger than the VOC mixing ration by 40% and 130% respectively.

The alkane mixing ratios were determined from summing up the m/z 57, 71, 85, 99, and 113 thermal desorption ion responses and applying the diesel fuel based sensitivity factor 1.5 Hz ppbv⁻¹ per MHz H₃O⁺. Uncertainty in the fuel based alkane sensitivity arises from uncertainty in the reported molar abundance of alkanes by carbon number (not well quantified in the literature), the potential for interfering ion fragments from other compound groups (thought to be
small), and in assuming that the molar abundance of C_{12-18} alkanes in fuel is similar to that found in exhaust. The calculated IVOC alkane mixing ratio of 150 ppbv is similar to the sum total of the C_{1-4} alkylbenzenes \((m/z\ 93, 107, 121, 135)\) mixing ratio of 198 ppbv. This data can be compared to that reported by Schauer et al (1999) where the molar ratio of the total C_{12} to C_{18} n-alkane emission rates to the reported C_{1-3} alkylbenzene compound emission rates was 0.20. In our experiment the ratio of the IVOC alkane mixing ratio to the total C_{1-3} alkylbenzene \((m/z\ 93, 107, 121)\) mixing ratios was 0.90. The difference could be attributed to the presence of isoalkanes that would be observed by the IVOC sampler, but were not reported by Schauer et al. (1999). It is also interesting to compare the alkylbenzene abundance to the other aromatic compound groups. The sum total of the major naphthenic monoaromatic compounds \((m/z\ 119, 133, 147, 161, 175)\) was 66 ppbv, and sum total of naphthalene group \((m/z\ 129, 143, 157)\) was 41 ppbv. Together these compounds account for about half the molar abundance of the more routinely measured VOC alkylbenzene compounds.

Figure 3.8 displays the IVOC thermal desorption peak area response for selected ions relative to that of \(m/z\ 135\). The \(m/z\ 135\) ion, attributed to C_{4-alkylbenzene} compounds, is abundant in both diesel and gasoline exhaust. A clear difference was observed between the diesel and gasoline exhaust relative abundance. In general, the gasoline exhaust ratios to \(m/z\ 135\) were a factor of 10 lower than the diesel exhaust, reflecting the larger mass emission rate of higher molecular weight compounds in diesel exhaust. The relative abundance pattern for each engine exhaust type can potentially be used as a source fingerprint to quantify the relative contributions of diesel and gasoline engine exhausts to organic compound concentrations in urban air. For this study, it was found that a mixture containing diesel and gasoline engine exhaust yielded compound abundance ratios between the two pure exhaust source ratios as
shown in the figure. The observed exhaust mixture ratio could be reasonably well estimated from the source ratios as defined by the following equations:

\[
R_i = (x \times D_i) + (y \times G_i)
\]  
(3.3)

\[
x + y = 1
\]  
(3.4)

where \(R_i\) is the observed ratio at \(m/z\) mass \(i\), \(D_i\) and \(G_i\) are the exhaust fingerprint ratios observed in the diesel and gasoline exhaust at mass \(i\), and \(x\) and \(y\) are the fractions of diesel and gasoline exhaust in the mixture. For example, the figure shows observed ratios of 50:50 mixture of diesel and gasoline engine exhaust and a fit based on equation 3.3 using \(x\) and \(y = 0.5\). The good agreement suggests there is the potential to quantify the relative contributions of diesel and gasoline engine exhausts in urban air using IVOC compound measurements by PTR-MS.

3.4. Conclusion

Analysis of gasoline and diesel fuel and gasoline and diesel engine exhaust was performed to determine if the PTR-MS instrument could be used to quantify long chain alkanes and other IVOC compounds associated with diesel exhaust emissions. Laboratory experiments show the PTR-MS sensitivity to \(n\)-alkanes increases with compound carbon number with negligible sensitivity to \(n\)-alkanes smaller than \(C_8\). For larger \(n\)-alkanes, the sensitivity is much less than expected if these compounds react at the collisional rate limit with \(H_3O^+\). Sensitivities do not increase with decreasing drift tube Townsend number, suggesting the proton transfer reaction with larger alkanes is endothermic. The \(n\)-alkanes fragment to a common set of ions with formula \(C_nH_{2n+1}\) as well as \(m/z\) 41. The relative intensity of the fragment ions was a function of drift field strength; at lower Townsend values more ion intensity occurred in larger masses and some branched alkanes yielded significant M-1 ions. Laboratory tests of fragmentation patterns imply that cycloalkanes \((C_nH_{2n+7}: m/z\ 69, 83, 97, 111, 125)\) and
naphthenic monoaromatics \((C_{n+9}H_{2n+11}: m/z 119, 133, 147 \text{ etc.})\) are important constituents in both fuel and exhaust. A diesel fuel based sensitivity factor of \(2.6 \text{ Hz ppbv}^{-1} \text{ per MHz H}_3\text{O}^+\) was calculated for \(C_{12}-C_{18}\) alkanes at 80 Td drift condition.

A thermal desorption sampler was added to the PTR-MS drift tube, allowing for normal VOC measurements as well as sample collection and desorption of heavier organics from a Tenax TA adsorbent. In this analytical approach the PTR-MS drift tube was operated at 80 Td for both VOC sampling and thermal desorption analysis to reduce fragmentation. The thermal desorption sampler discriminated against VOC compounds by using a high temperature purge before direct desorption into the PTR-MS drift tube using dry \(N_2\) carrier gas. By implementing a purge, VOC compounds that would interfere with the measurement of \(C_{12} - C_{18}\) long chain alkanes were removed. In diluted diesel engine exhaust IVOC alkane mixing ratios were measured to be 76\% of the sum total of \(C_1-C_4\) alkylbenzene abundance, and therefore comprise a significant amount of precursor material for secondary organic aerosol formation. Thermal desorption sampling and low Townsend number PTR-MS analysis is a viable approach for providing quantitative information on the total abundance of long chain alkanes and aromatics species in diesel exhaust. While diesel and gasoline engine exhaust composition of volatile components were similar, the ratios of IVOC compounds to \(m/z 135\) were quite different. These ratios may allow for emission profiles to be developed to better quantify the relative contributions of diesel and gasoline exhaust emissions to urban air concentrations of organic compounds.
3.5. References


3.6. Tables and Figures

Table 3.1: Percent of total ion signal for the different groups in diesel and gasoline fuels.

<table>
<thead>
<tr>
<th>Compound Group</th>
<th>Mass Formula</th>
<th>Base Ion</th>
<th>Major m/z</th>
<th>Diesel</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Td=120</td>
<td>Td=80</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Td=120</td>
<td>Td=80</td>
</tr>
<tr>
<td>alkanes</td>
<td>CₙH₂n+1</td>
<td></td>
<td>43, 57, 71, 85, 99, 113, 127,</td>
<td>43.3%</td>
<td>23.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>141, 155, 169</td>
<td>17.1%</td>
<td>17.7%</td>
</tr>
<tr>
<td>cycloalkanes</td>
<td>CₙH₂n-1</td>
<td>M-1</td>
<td>69, 83, 97, 111, 125, 139,</td>
<td>8.2%</td>
<td>8.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>153, 167, 181</td>
<td>10.5%</td>
<td>20.1%</td>
</tr>
<tr>
<td>Unknown (bicycloalkanes)</td>
<td>Cₙ₊₅H₂n+7</td>
<td>M-1</td>
<td>123, 137, 151, 165, 179, 193</td>
<td>7.4%</td>
<td>14.3%</td>
</tr>
<tr>
<td>alkylbenzenes</td>
<td>Cₙ₊₆H₂n+7</td>
<td>M+1</td>
<td>79, 93, 107, 121, 135, 149,</td>
<td>0.8%</td>
<td>1.7%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>163, 177, 191</td>
<td>0.8%</td>
<td>1.7%</td>
</tr>
<tr>
<td>naphthenic monoaromatics</td>
<td>Cₙ₊₉H₂n+11</td>
<td>M+1</td>
<td>119, 133, 147, 161, 175, 189,</td>
<td>88%</td>
<td>87%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>203</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dihydro-naphthalenes</td>
<td>Cₙ₊₁₀H₂n+11</td>
<td>M+1</td>
<td>131, 145, 159, 173, 187, 201</td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphthalenes</td>
<td>Cₙ₊₁₀H₂n+9</td>
<td>M+1</td>
<td>129, 143, 157, 171, 185</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sum of ion signal</td>
<td></td>
<td></td>
<td></td>
<td>88%</td>
<td>87%</td>
</tr>
</tbody>
</table>
Table 3.2: Comparison of Fuel and Exhaust Composition at 80 Td.

<table>
<thead>
<tr>
<th>Group</th>
<th>Formula</th>
<th>Measured m/z</th>
<th>Diesel Fuel</th>
<th>Diesel Exhaust</th>
<th>Gasoline Fuel</th>
<th>Gasoline Exhaust</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygenated</td>
<td></td>
<td>31,33, 45,47,59</td>
<td>19.7%</td>
<td>50.3%</td>
<td>45.1%</td>
<td>51.1%</td>
</tr>
<tr>
<td>alkanes / alkenes</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;2n+1&lt;/sub&gt;</td>
<td>43,57,71,85,99,113,127</td>
<td>20.3%</td>
<td>19.4%</td>
<td>20.6%</td>
<td>16.4%</td>
</tr>
<tr>
<td>cycloalkanes</td>
<td>C&lt;sub&gt;n&lt;/sub&gt;H&lt;sub&gt;2n-1&lt;/sub&gt;</td>
<td>69,83,97,111,125,139</td>
<td>15.3%</td>
<td>4.3%</td>
<td>3.6%</td>
<td>3.3%</td>
</tr>
<tr>
<td>alkylbenzenes</td>
<td>C&lt;sub&gt;n+6&lt;/sub&gt;H&lt;sub&gt;2n+7&lt;/sub&gt;</td>
<td>79, 93,107,121,135, 149, 163, 177, 191</td>
<td>21.9%</td>
<td>22.3%</td>
<td>28.6%</td>
<td>26.6%</td>
</tr>
<tr>
<td>unknown (bicycloalkanes)</td>
<td>C&lt;sub&gt;n+5&lt;/sub&gt;H&lt;sub&gt;2n+7&lt;/sub&gt;</td>
<td>81, 95, 109, 123, 137, 151, 165</td>
<td>6.1%</td>
<td>2.5%</td>
<td>0.3%</td>
<td>1.3%</td>
</tr>
<tr>
<td>naphthenic</td>
<td>C&lt;sub&gt;n+9&lt;/sub&gt;H&lt;sub&gt;2n+11&lt;/sub&gt;</td>
<td>119, 133, 147, 161, 175, 189</td>
<td>15.1%</td>
<td>0.9%</td>
<td>0.9%</td>
<td>1.0%</td>
</tr>
<tr>
<td>monoaromatics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>naphthalenes</td>
<td>C&lt;sub&gt;n+10&lt;/sub&gt;H&lt;sub&gt;2n+9&lt;/sub&gt;</td>
<td>129, 143, 157, 171</td>
<td>1.6%</td>
<td>0.3%</td>
<td>0.8%</td>
<td>0.3%</td>
</tr>
</tbody>
</table>
Figure 3.1: PTR-MS raw mass spectrum of dodecane (C$_{12}$H$_{26}$) at 120 Td (upper panel) and 80 Td (lower panel) drift tube conditions. A clear pattern of C$_n$H$_{2n-1}$ ion fragments is evident. At 80 Td the M-1 ion ($m/z$ 169) is more intense. The $m/z$ 189 ion is attributed to the M•H$_3$O$^+$ cluster.
Figure 3.2: n-Alkane sensitivity (left axis) for 120 Td (blue squares) and 80 Td (green circles) compared to measured $\text{H}_3\text{O}^+$ + n-alkane rate coefficients (black diamonds) by Arnold et al., (1998) expressed as a percentage of collision rate limit (right axis). Also shown is the proton affinity (red triangles) determined by Hunter and East (2002).
Figure 3.3: PTR-MS mass spectrum of diesel fuel #2 at 120 Td (panel A) and 80 Td (panel B) and gasoline at 120 Td (panel C) and 80 Td (panel D). Ion signal has been color coded to assign ions to common fragmentation patterns that identify common organic compound classes.
Figure 3.4: Examination of the C_{12}-C_{14} compound range ion signal pattern for diesel fuel. Peaks have been tentatively identified as belonging to 1 of 7 compound groups that differ by the degree of unsaturation, ranging from naphthalenes to alkanes.
Figure 3.5: PTR-MS mass spectrum of gasoline exhaust (top) and diesel exhaust (bottom) at 80 Td. Ion signal has been color coded to assign ions to common fragmentation patterns that identify common organic compound classes: alkane fragment ions (black), alkylbenzenes (blue), cycloalkane fragment ions (green) and naphthenic monoaromatics (red).
Figure 3.6: Time series of measurements showing VOC and IVOC signals in gasoline (left) and diesel (right) exhaust. The IVOC mode signal is indicated by the grey shaded area. The ion signal (Hz) is normalized to MHz H$_3$O$^+$. 
Figure 3.7: Diluted diesel exhaust mixing ratios illustrating abundance of compounds measured by the PTR-MS by VOC (solid bars) and IVOC (striped bars) sampling modes.
Figure 3.8: PTR-MS IVOC mode exhaust fingerprints observed for diesel exhaust (blue squares), gasoline exhaust (red circles), and an approximately 50:50 mixture (green diamonds). The dashed line is a calculated exhaust fingerprint of a 50:50 mixture of gasoline and diesel exhaust given the source profiles shown. Color bands indicate compound group: alkane fragment ions (grey), alkylbenzenes (blue); cycloalkane fragment ions (green), naphthenic monoaromatics (red), and bicycloalkanes (orange).
4.1. Abstract

PTR-MS measurements during the Carbonaceous Aerosols and Radiative Effects Study (CARES) in June 2010 in Sacramento are presented here. The PTR-MS was outfitted with two custom built sampling methods: one to remove water vapor to increase sensitivity of VOC species (dehumidifier) and another to quantify the abundance of IVOC species (IVOC sampler). The observations utilizing the dehumidifier showed biogenic (evidenced by isoprene trends), anthropogenic (evidenced by alkylbenzenes), and oxidation (evidenced by formaldehyde, methacrolein, and methyl vinly ketone trends) influences at the site. The IVOC sampler quantified the abundance of C_{10}-C_{17} IVOC alkanes, which were determined from the sum of m/z 57, 71, 85, and 99 ions. The IVOC alkanes were about 40% less abundant than the alkylbenzenes (m/z 79, 93, 107, 121) on average and a few large pollution events resulted in IVOC alkanes of nearly 3 ppbv. Two pollution events starting on the 16th and 20th of June saw transport of vehicle emissions from Interstate Highway 80 and allowed for comparison of the IVOC alkanes to other vehicle exhaust tracers. The IVOC alkane concentrations were 30 to 40 times higher than soot and 3 to 5 times higher than organic aerosol mass concentrations. There was a strong correlation between the IVOC alkanes and soot, providing evidence that the IVOC alkanes could be attributed to diesel vehicle exhaust. This suggests there is a significant abundance of IVOC species from vehicle emissions and potentially a significant pool of reactive compounds that could be important SOA precursors.
4.2. Introduction

During June, 2010 the PTR-MS measurement method was used during the Carbonaceous Aerosols and Radiative Effects Study (CARES) that took place in Sacramento, CA (Zaveri et al., 2012). As detailed in section 1.4, one goal of the CARES experiment was to study how SOA and SOA precursors interact in an urban environment (Zaveri, et al., 2012). A few manuscripts have published results from CARES. Fast et al. (2012) looked at the transport and mixing patterns of the area. Setyan, et al. (2012) characterized the submicron particles with a high-resolution aerosol mass spectrometer. The Research at the Nexus of Air Quality and Climate Change (CalNex) study overlapped with CARES and Cahill, et al. (2012) analyzed the aerosol particle mixing state based on data from both studies. Shilling, et al. (2013) studied how mixtures of anthropogenic and biogenic emissions effect SOA formation. The PTR-MS was deployed with the dehumidifier and IVOC sampler to quantify urban VOC and IVOC abundances. Both approaches were field tested in an urban setting as part of CARES and are presented here.

4.3. Experimental

4.3.1. Site Characteristics

The PTR-MS was stationed at the T0 site at American River College in Sacramento, CA and housed in WSU Laboratory for Atmospheric Research’s Mobile Atmospheric Chemistry Lab (MACL) with other instrumentation. The general location of the site is marked on the map viewed in Figure 4.1. A large number of instruments were deployed at T0 in two other instrumented trailers to measure both gas and particle phase compounds at this site (Zaveri et al., 2012). The instrumentation operated from June 2 through June 28 except the IVOC sampler, which collected data from June 13 to June 29. The IVOC sampler inlet line consisted of a heated
0.0375 cm (1/8”) OD electropolished stainless steel tubing (UHP Cardinal) with the inlet 3.4 m above ground. A 2 µm Teflon filter was attached to the inlet to remove particles. A flow of 1 slpm was pulled through the line. It was heated to 80 °C and the PTR-MS subsampled from this flow to collect an IVOC sample. VOCs were measured by subsampling from a 1.27 cm (½”) PFA inlet line mounted on MACL’s 10-m crank up tower at a height of 9-m. The VOC sample was dehumidified by passing through a cold tube at -30 °C (Jobson and McCoskey, 2010). A Single Particle Soot Photometer (SP2), a Scanning Mobility Particle Sizer (SMPS), and a High Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) sampled from a high flow aerosol inlet described by Zaveri et al. (2012).

4.3.2. Instrumentation

A number of instruments were deployed to measure trace gases, solar radiation, meteorology, and particle composition, concentration and physical properties. A more detailed description of the instrumentation was reported by Zaveri et al. (2012). This report utilizes the data from the Ionicon PTR-MS (VOCs), AeroLaser AL5002 Fast CO Analyzer (CO), Dasibi 1008-PC Ozone Monitor (O₃), Air Quality Design NOₓ analyzers (NO, NOₓ, NOᵧ), Aerodyne AMS (organic aerosols), Droplet Measurement Technologies SP2 (soot), ThermoElectron Model 43I (SO₂), Vaisala WXT-510 Meteorological Station (temperature, pressure, wind speed, wind direction, relative humidity), and a TSI SMPS (particle count). The PTR-MS is outfitted with a dehumidifier (section 4.3.2.1) to enhance measurement of VOC species and an IVOC sampler (section 4.3.2.2) to measure IVOC species.

4.3.2.1. Dehumidifier VOC Sampling

The removal of water vapor from the sample allows for operation at lower Townsend numbers, which provides a number of benefits. The lower Townsend number means a longer...
reaction time, which leads to higher sensitivity through more collisions and lower fragmentation due to decreased kinetic energy. The VOC sample is dried by passing the sample through a -30 °C cold tube as described in Jobson and McCoskey (2010). The cold trap also removes IVOC species through physical adsorption to the cold ice surface. The dehumidifier is outfitted with two 1/4” outer diameter ResTek tubes that are encased in an aluminum block that is cooled to -50 °C. The tubes are temperature controlled using temperature controllers (Watlow) whose temperature set points are controlled by an external program to automate operation of the water trap (DaqFactory, Azeotech). There are three different states the tubes undergo: sample, backflush, and condition. The PTR-MS sampled from each tube for 30 minutes at ~250 sccm. During this time the other tube is backflushed and conditioned. The backflush entails the tube being heated to 65 °C and flushed with dry nitrogen for 10 minutes. Then the tube is cooled and the traps are conditioned by pulling ~250 sccm of air through the cold tube for 20 minutes at -30 °C. The PTR-MS then switches to sampling through the newly conditioned tube and the other tube goes through the same backflush and conditioning. For this set-up, the -30 °C trap temperature sampling allows transmission of oxygenated compounds like formaldehyde, CH₃OOH, methanol, and acetone. Significant losses of larger alkylbenzenes compounds (i.e. ≥ C₄-alkylbenzenes) at low mixing ratios less than 100 pptv is known to occur (Jobson and McCoskey, 2010). The system was calibrated using a tank standard (Scott-Marrin, ±5% accuracy) and backgrounds were determined by generating zero air through cleaning room air with a Pt catalyst.

One of the main factors in the development of the dehumidifier was to increase our ability to quantify formaldehyde with the PTR-MS. The proton affinity of formaldehyde is 713 kJ mol⁻¹, which is slightly above H₂O at 697 kJ mol⁻¹. The proton transfer reaction between
H$_3$O$^+$ to formaldehyde (HCHO) will be exothermic, but since the proton affinities are so close there is enough energy present in the drift tube to drive the endothermic back reaction to transfer the proton from formaldehyde back to H$_2$O. This results in the formaldehyde sensitivity being largely dependent upon the amount of water vapor present in the sample, with higher water vapor concentrations leading to more back reactions. With implementation of the dehumidifier, the water vapor is greatly reduced, which in turn reduces the back reactions and ultimately increases the formaldehyde signals leading to higher sensitivity and lower detection limits. This relationship and fidelity of the dehumidifier is further explained by Jobson and McCoskey (2010).

4.3.2.2. Thermal Desorption IVOC Sampler

Due to the low concentrations of IVOCs in the atmosphere, preconcentration is required for detection by the PTR-MS instrument. A thermal desorption sampling methodology was used for IVOC sample collection. Section 2.2 contains a detailed description of the IVOC sampler. The C$_8$ and heavier alkanes undergo dissociative proton transfer reactions in the PTR-MS (Jobson et al., 2005) producing C$_n$H$_{2n+1}$ for $n \geq 3$ fragmentation patterns seen in electron impact ionization. The C$_7$ and lighter alkanes show little to no response within the PTR-MS. While larger n-alkanes display an increasing sensitivity with carbon number, their PTR-MS sensitivity is much lower than expected for a compound reacting at the collision rate limit with H$_3$O$^+$, suggesting their proton affinities are less than that of H$_2$O (section 3.3.1). The PTR-MS was operated at 80 Td, which improves the instrument sensitivity and eliminates fragmentation of many compounds found in urban air. This also shifts the alkane fragmentation towards the heavier ions which reduces potential interference from fragmenting VOC species since $m/z$ 43 and 57 are common fragment ions. By shifting the alkane signal towards larger ions ($m/z$ 85, 99,
113, etc.) through 80 Td operation there is lower potential for positive interferences from VOC compounds. The relative intensity of the alkane fragment ions varies with compound structure, with branched and iso-alkanes often yielding a significant (up to 45%) M-1 ion. Due to the complexity of the fragmentation patterns and the unknown composition of IVOC alkane isomers in urban air, the PTR-MS response to alkanes was calibrated using diesel fuel as described in section 3.3.5. Diesel fuel contains a complex mixture of alkanes whose molar abundance by carbon number has been reported by Gentner et al. (2012). We assume the fuel distribution is reasonably similar to exhaust and urban air. The sensitivity of alkanes in diesel fuel was 5.1 ncp/s or 2.73x10^5 area counts nmol⁻¹.

In the CARES study sample collection onto the Tenax adsorbent took 30 minutes at a flow rate of 40.5 sccm. Desorption took 5 minutes at a flow rate of 24 sccm of UHP N₂ into the drift tube. The Tenax was kept at 30 °C during the first 27 minutes of sampling and at 100 °C for the last 3 minutes to remove volatile components from the trap that produce interfering ions for the measurement of alkanes, such as C₃-C₆ alkenes, methacrolein, methyl vinyl ketone and other compounds. Lab tests have shown that by increasing the Tenax temperature to 100 °C during the last three minutes of sampling the removal of methacrolein, benzene, toluene, p-xylene, 1,2,4-trimethylbenzene, 1,2,3,5-tetramethylbenzene, and alpha pinene was 99%, 88%, 58%, 25%, 20%, 21% and 93% respectively. The breakthrough volumes of n-heptane, n-heptene, and pentanal are similar to benzene, so removal of < C₈ alkanes and alkenes and < C₆ aldehydes will be also achieved. Given the sensitivity of alkanes in the PTR-MS and the removal of < C₈ alkanes, the IVOC sampler measures C₁₀ to C₁₇ alkanes. It is important to note that this purge method is different than described in chapters two and three and does not discriminate to a high enough degree to get rid of all VOCs and the desorption temperature was
180 °C. After the desorption was complete, the adsorbent trap was heated to 200 °C and backflushed with 104 sccm dry N\textsubscript{2} flow for 4 minutes. After the backflush period, the IVOC system was returned to sampling mode. The measurement of VOCs was implemented during the sampling and backflushing modes. During desorption, a total of 120 mL passed through the Tenax trap. At 180 °C, the breakthrough volumes of dodecane, heptadecane, and octadecane are 17, 110, and 180 mL respectively. This means that there is sufficient volume to allow for complete desorption of C\textsubscript{17} and lower alkanes but C\textsubscript{18} and larger alkanes will not be completely desorbed from the trap. During desorption, the trap was heated from 100 °C to 180 °C in 24 seconds. The result was a desorption peak, an ion count rate versus time signal, whose area (total counts) was proportional to the mass collected on the adsorbent. Zero air was collected on the trap in the same manner as a sample and peak responses above the zero air signal were determined. No significant contamination or sample carry-over was observed. The selected ions measured for the thermal desorption analysis were different than the VOC mode. In the IVOC analysis the following ions were measured to assess abundance of different functional groups: \(m/z\) 57, 71, 85, and 99 (alkanes); \(m/z\) 93, 121, and 135 (alkylbenzenes); 97, 111, 125, and 139 (cycloalkanes); \(m/z\) 143 (methylnaphthalene); and \(m/z\) 161 (naphthenic monoaromatic).

4.3.3. Meteorological Data

The 10-m air temperature, pressure, relative humidity, wind direction and wind speed measured at T0 during CARES are plotted in Figure 4.2. Shown are 1 minute averages for relative humidity, pressure and temperatures and 30 minute averages for wind speed and direction. The temperature ranged from 11 °C to 39 °C, with peak temperatures during the day being 30 °C and night temperatures dropping to 15 °C on average. The pressure remained fairly stable during the course of measurements ranging from 1001 to 1017 mbar with an average
pressure of 1009 mbar. The relative humidity followed a fairly consistent pattern, typically reaching approximately 25% during the day and 75% at night. The wind direction was typically from the south to southwest except for the 10th to 14th, 16th and 17th, and 20th to 22nd where winds were from the north to northwest. The wind speed was typically below 4 m s\(^{-1}\) except during the northern wind periods which coincided with higher wind speeds.

The northwest winds on the 16th-17th and 20th-22nd coincided with increased pollution at the T0 site. Fast et al. (2012) provided a detailed analysis of meteorological data during the CARES campaign. These events saw wind coming from the Sacramento Valley to the northwest. Interstate Highway 80 is also located to the northwest of the site, which means that vehicle emissions will be a large source, which coincides with the observations of increased pollution. The pollution events from the 16th-17th and 20th-22nd provided the fullest data sets for analysis and will be referred to as PE 17 and PE 20.

4.4. Results

4.4.1. CO, NO\(_X\), SO\(_2\), O\(_3\)

The CO, NO\(_X\), SO\(_2\), and O\(_3\) mixing ratios measured at T0 are plotted in Figure 4.3. Shown are 1 minute averages. There were a number of CO plumes that exceeded 500 ppbv, but the CO levels were typically below 300 ppbv. NO\(_X\) levels were typically below 20 ppbv with a number of daily maximums exceeding 30 ppbv. The pollution events (PE 17 and PE 20) are apparent in the CO, NO\(_X\), and O\(_3\) data. The CO was an average of 575 ppbv over an 8 hour period during PE 17 and reached a maximum of ~500 ppbv during PE 20. NO\(_X\) reached its highest mixing ratios during these events, with the NO effectively titrating away O\(_3\). The SO\(_2\) behaved much differently, with mixing ratios near detection limits during PE 17 and PE 20, but showing increased values before, in between and after PE 17 and PE 20. SO\(_2\) ranged from zero
to ~1 ppbv, but saw abundances above 1 ppbv for extended periods of time when winds were from the southwest on the 14th and 15th, 18th and 19th, and the 26th through 25th. During these periods, Fast et al. (2012) reports southwesterly winds and the refineries located along the Carquinez Strait as the source of SO$_2$. O$_3$ followed the expected diel pattern, reaching a value of 60 ppbv on average during the day with an observed maximum abundance of 115 ppbv occurring on the 28th, which also saw the highest temperatures.

4.4.2. PTR-MS VOC Data

4.4.2.1. Aromatics

The aromatic compounds are considered vehicle exhaust tracers, being major components of gasoline fuel and gasoline and diesel exhaust (Schauer et al., 1999; Schauer et al., 2002). The $m/z$ 79, 93, 107, 121, and 135 ions were monitored through the dehumidified VOC method. Figure 4.4 is a timeseries of these species over the entire campaign. Toluene ($m/z$ 93) and the C$_2$-benzenes ($m/z$ 107; xylenes, ethylbenzene) showed the highest concentrations, reaching around 2 ppbv during PE 17, over 1 ppbv during PE 20 and over 2 ppbv on the 28th.

All of the aromatics followed the same trend, indicating a common source. Linear correlations between aromatic compounds and toluene are shown in Figure 4.5. The strongest correlations were found with the C$_2$-benzenes ($m/z$ 107) and C$_3$-benzenes ($m/z$ 121) with $r^2$ values of 0.88 and 0.86 respectively. Benzene ($m/z$ 79) and C$_4$-benzenes ($m/z$ 135) showed lower, but good correlations, with $r^2$ values of 0.69 and 0.68 respectively. The poorer correlations of the benzene and C$_4$-benzenes with toluene is partially due to the lower mixing ratios observed for these compounds. There were periods when benzene or C$_4$-benzenes were at the instrument detection limit producing variability due to instrument noise. Nonetheless, with the high correlations and the abundance of aromatics within vehicle exhausts, it points towards
vehicles being the major source of pollution during the course of the campaign. This notion is consistent with the knowledge of the urban surroundings and proximity of Interstate 80 to the northwest.

4.4.2.2. HCHO and MHP

The left panel of Figure 4.6 is a timeseries of ozone, formaldehyde and methylhydroperoxide (CH$_3$OOH) measured during the campaign. It can be noted that the three follow the same trends and behave as expected of photoproducts with the mixing ratios increasing steadily throughout the day and decreases at night. The formaldehyde was present in much larger quantities with mixing ratios peaking around 5 ppbv during most days. Being a less common product during photooxidation, the methylhydroperoxide mixing ratios are approximately 10 times lower than formaldehyde. Plotting methylhydroperoxide versus formaldehyde yielded a reasonable correlation with an $r^2$ value of 0.82. This suggests that they are from a similar source, which points towards photooxidation being the main source of both species. However, there is not a good correlation between formaldehyde and ozone ($r^2 = 0.29$) even though they are both photoproducts. This difference is due to the different sources and formation pathways.

4.4.2.3. Biogenics

While the main sources of pollution are expected to be anthropogenic, there is also a large biogenic influence in the area from surrounding forests and urban vegetation, with isoprene being a major biogenic emission. Figure 4.7 displays isoprene ($m/z$ 69) and monoterpenes ($m/z$ 137) during the campaign. As expected given the light and temperature dependence of isoprene emission rates, the isoprene mixing ratio follows a diel pattern, reaching its peak concentrations during the afternoons with highest temperatures. Both $m/z$ 69 and $m/z$ 137 increased on the 14th,
when CO remained relatively low. This coincides with increases in m/z 71 which is influenced by the response of isoprene photoproducts. This suggests that the site was under heavy biogenic emission influence on the 14th. However, during PE 17, PE 20, and on the 28th, there was a large response at m/z 69 at night. Isoprene emissions are light dependent, so this increase at night would not suggest biogenic sources during these pollution events. As seen in Figure 4.8, the isoprene reached near zero on the night of the 15th and 17th. However, m/z 69 stayed elevated throughout the night of the 16th during PE 17. It is unclear what causes this response, but Section 3.3.2 showed that cycloalkane fragmentation generates a response at m/z 69, so the response could be due to vehicle exhaust. This could be an important interference in urban environments, possibly leading to overestimation of isoprene.

The monoterpenes were relatively low during a majority of the observations. Monoterpene mixing ratios are often highest during nighttime due to a shallow mixing layer, which would point to biogenic emissions. They do not appear to be following this pattern. In fact, the response at m/z 137 appears to be more anthropogenic in nature, with a noticeable response during PE 17, PE 20, and on the 28th. Previous work has shown that bicycloalkanes in vehicle emissions generate a response at m/z 137 (Section 3.3.3). The ratio of m/z 137 to 93 during PE 17 was 0.55. Measurements of diesel and gasoline exhaust in chamber experiments at LRRI resulted in ratios of 0.19 for diesel exhaust and 0.0047 for gasoline exhaust. The CARES ratio was more than twice as high as the ratio in diesel exhaust and about a factor of 100 higher than the gasoline exhaust ratio. This suggests that the response at m/z 137 is likely a mixture of monoterpenes and vehicle exhaust.
4.4.2.4. Photoproducts

Figure 4.7 shows a few of the other ions where photoproduct response is typically found. The $m/z$ 45, 71, and 73 are typical ions that see responses from acetaldehyde, methacrolein (MACR) + methyl vinyl ketone (MVK), and methyl ethyl ketone (MEK) respectively. All of them are photoproducts that are typically observed in urban environments. Isoprene oxidation results in the formation of formaldehyde, MACR and MVK as the major first generation oxidation products. Abundance of these compounds should be related to the abundance of isoprene, and if isoprene oxidation is the major source of these compounds, then $m/z$ 31 (formaldehyde) and $m/z$ 71 (MACR + MVK) should be well correlated. Figure 4.9 shows the time-series of $m/z$ 31, 69, and 71 for June 4th to the 13th. Winds were generally from the west and southwest from the 3rd to the 9th and roughly from the north from the 10th to 14th (Fast et al., 2012). All three species see diel patterns during this time and the correlation between $m/z$ 31 and $m/z$ 71 yielded an $r^2 = 0.63$, suggesting the oxidation of isoprene as the major source.

Acetaldehyde mixing ratios were about half of that observed for formaldehyde, with MEK even lower. The large increases in acetaldehyde during PE 17, PE 20, and on the 28th are attributed to vehicle emissions, in which acetaldehyde is among the major constituents of exhaust (Schauer et al., 1999; Schauer et al., 2002). There also appeared to be increased photochemical activity on the 14th, with $m/z$ 45, 71, and 73 seeing increases with little response from CO.

Another photoproduct of interest can respond at $m/z$ 139. This is often the response of nopinone, which is a product of the ozone initiated oxidation of beta-pinene. Looking at Figure 4.7 it can be noted that the response is not behaving like a photoproduct, but is high during PE 17, PE 20, and on the 28th. This response may be attributed to cycloalkanes and aldehydes in
vehicle exhaust that have been reported to respond at \( m/z \) 139 (Section 3.3.2), but at least suggests the response is influenced by anthropogenic emissions.

4.4.2.5. Solvent and Fire Tracers

Methanol, acetonitrile, and acetone respond at \( m/z \) 33, 42, and 59 respectively. Figure 4.10 is shows the response for these species over the course of measurements. The methanol and acetone follow a similar trend to the VOCs with increases during PE 17, PE 20, and on the 28th. They also saw a large increase during what appears to be a biogenic plume on the 14th. This suggests that there were both biogenic and anthropogenic sources generating a response at these ions. Minimal response was observed in acetonitrile (\( m/z \) 42) during CARES. The major source of acetonitrile is wood burning and is elevated in wildfire plumes and residential wood combustion emissions. No acetonitrile was expected since there is no residential heating by wood combustion during summer and no wildfires occurred during the observation period.

4.4.3. PTR-MS IVOC Data

4.4.3.1. Aromatics

Based on their abundance in the diesel fuel mass spectrum, a series of ions were selected for monitoring in the CARES field campaign. The ions \( m/z \) 93, 121 and 135 were selected to measure alkylbenzene abundance with the intention of comparing the IVOC response for these ions to the VOC mode response. To compare the IVOC to VOC data, an IVOC sensitivity was calculated from the VOC sensitivity determined during periodic calibrations. The sensitivities for \( m/z \) 93, 121, and 135 were 17, 14, and 13 ncps respectively, which translate into IVOC sensitivities of \( 4.4 \times 10^5 \), \( 3.1 \times 10^5 \), and \( 8.5 \times 10^4 \) area counts nmol\(^{-1}\) respectively. A plot of IVOC measured \( m/z \) 93 vs. VOC measured \( m/z \) 93 yielded a slope of 0.58 and an \( r^2 \) of 0.60 resulted (Figure 4.11). If the systems are in agreement, the slope would be expected to be 1:1, but the
observed slope is much lower. This was due to the discrimination against toluene, which is typically attributed to the response at $m/z$ 93, during the IVOC sampler purge mode. Given this, the discrimination against toluene during CARES would be estimated at 40%. This was different than the lab results, which suggests less discrimination occurred during field sampling.

The same approach was performed for $m/z$ 121 (C$_3$-alkylbenzenes) and $m/z$ 135 (C$_4$-alkylbenzenes). The comparison of IVOC and VOC $m/z$ 121 resulted in a slope of 1.09 at an $r^2$ of 0.48. There was better agreement with the IVOC sampler observing slightly higher mixing ratios and would suggest that there was a negligible amount of discrimination against C$_3$-alkylbenzenes, which is consistent with the field discrimination being less than observed in the laboratory. The slope of 3.02 observed for the $m/z$ 135 response showed a much larger difference between the two sampling methods. This difference may be attributed in part to fragmentation of larger alkylbenzenes or the increased fidelity of the IVOC sampler to measure larger alkylbenzenes. However, this difference may primarily be due to substantial losses to tubing and the -30 °C cold zone during VOC dehumidifier sampling. Conversely, the IVOC sampler contained a shorter, heated inlet that facilitated better transmission of heavy alkylbenzenes through the sample lines, resulting in much higher observed mixing ratios.

4.4.3.2. Alkanes

The ions $m/z$ 57, 71, 85, and 99 (C$_n$H$_{2n+1}$) were chosen to measure the alkane abundance. The area count response for these ions together with NO$_x$ mixing ratios averaged over the IVOC sampling time are shown in Figure 4.12. In general the ions covaried with each other and tracked variations in NO$_x$. It was noted earlier that $m/z$ 71 has a large response from isoprene oxidation and can often follow a diel pattern. If the IVOC sampler was not efficiently removing $m/z$ 71 photoproducts (methacrolein and methyl vinyl ketone) the IVOC signal would follow the
same diel pattern. Figure 4.13 shows a time-series of \( m/z \) 69 (isoprene), \( m/z \) 31 (formaldehyde), and \( m/z \) 71 (methacrolein, methyl vinyl ketone) mixing ratios along with the IVOC area counts observed at \( m/z \) 71. The \( m/z \) 31, 69, and 71 ions responded as one would expect from biogenic emissions, but the IVOC \( m/z \) 71 area counts do not follow this trend. No signal was observed at the IVOC \( m/z \) 71 when the other species were at their peak. The IVOC sampler was efficiently removing \( m/z \) 71 photoproducts (methacrolein and methyl vinyl ketone) so the IVOC signal did not follow the same diel pattern. This is evidence that the discrimination is working as intended and removing methacrolein and methyl vinyl ketone from the Tenax before measurement. The \( m/z \) 99 ion displayed the overall highest count rates, with the largest count rates occurring during a pollution episode on June 28.

The IVOC alkane concentrations were calculated from the sum of \( m/z \) 57, 71, 85, and 99 ions signal intensity using a sensitivity calculated using diesel fuel. The resulting alkane mixing ratio time-series is displayed in Figure 4.14 along with total alkylbenzene mixing ratio (\( m/z \) 79, 93, 107, 121) measured by the PTR-MS in VOC mode. These ions are attributed to benzene, toluene, \( \text{C}_2 \)-alkylbenzenes (xylenes and ethylbenzene) and \( \text{C}_3 \)-alkylbenzenes (trimethylbenzene isomers, ethyltoluene isomers, propylbenzene isomers), and are good tracers of spark ignition vehicle exhaust and important SOA precursors. The total alkane mixing ratio determined by this approach was very similar to the measured VOC alkylbenzene mixing ratios (\( m/z \) 79, 93, 107, 121) with the alkanes being approximately 40% lower on average.

Figure 4.15 shows the correlation of alkane to alkylbenzene mixing ratios observed during CARES. There was a reasonable correlation (\( r^2 \) of 0.56) between the IVOC alkanes and VOC alkylbenzenes (\( m/z \) 97, 107, 121); the data were bounded by alkane to alkylbenzene ratio limits of 0.10 and 3.65. The average alkane to alkylbenzene ratio was 0.87 ± 0.69 and the
median ratio was 0.72. The total IVOC alkane concentration calculated implies a substantial and important pool of carbon for SOA formation.

This alkane to alkylbenzene ratio can be compared to that observed in the traffic tunnel studies of Zeilinska et al., (1996). In that study C_{10}-C_{15} n-alkanes were measured, a reasonably proxy for the IVOC alkanes. The sum of these n-alkanes to toluene mixing ratios was found to yield a ratio of ~0.1 in a tunnel dominated by spark ignition vehicle traffic and 0.61 in a tunnel dominated by diesel traffic. The CARES data yields an average alkane (ppbv) to toluene (ppbv) ratio of 2.17. However, the ratios during PE 17 and PE 20 were 1.12 and 1.68 respectively. The PTR-MS is sensitive to branched IVOC alkanes and thus quantifies the total IVOC alkanes abundance so this ratio should be higher than that measured by Zeilinska et al. (1996). If diesel fuel can be used as a surrogate for n-alkane and branched alkane relative abundances in exhaust, data reported by Gentner et al. (2012) provides a means for use to estimate an n-alkane to toluene ratios, which will allow for better comparison to Zeilinska et al. (1996).

Gentner et al. (2012) reported C_{10}-C_{18} n-alkanes and some C_{10}, C_{11}, and C_{13} branched alkanes. Calculating a molar abundance from these species resulted in the C_{10}-C_{18} n-alkanes accounting for ~80% of the alkane composition. The ratios during PE 17 and PE 20 can be adjusted to be 0.93 and 1.39, which results in ratios that are closer to Zielinska et al. (2012), but still a factor of 1.5 to 2.3 higher. This ratio may still be high due to Gentner et al. (2012) not reporting every branched alkane within the diesel fuel. It is also likely that due to reductions in spark ignition exhaust emissions that any measure of diesel exhaust gas phase organics to spark ignition exhaust gas phase organic abundances will be higher now than in the mid 1990’s.
4.4.3.3. Cycloalkanes

The m/z 97, 111, 125, and 139 ions were monitored to assess cycloalkane abundance and their response is displayed in Figure 4.16 along with measured mixing ratios of C$_2$- and C$_3$-alkylbenzenes measured in VOC mode. We note that nopinone, a product of the ozone reaction with β-pinene, also occurs at m/z 139 and may be an interferent. The IVOC system does discriminate against C$_5$ and smaller aldehydes, but aldehydes up to C$_8$ have been reported in exhaust leading to potential interference (Schauer et al., 1999; Schauer et al., 2002). There was significant signal for the m/z 97, 111, and 125 ions. These ions were observed in both diesel fuel and gasoline and may be unique tracers of engine exhaust as there are few VOC species that produce ions at these masses in the PTR-MS. In general there was a good correlation between these masses and they displayed a similar pattern of variability as the C$_n$H$_{2n+1}$ ion group associated with alkanes. The m/z 97 ion displayed the largest response of this group. Elevated counts for all these ions were observed during PE 17, PE 20, and on the 28th corresponding to periods of elevated NO$_x$ and C$_2$ and C$_3$- alkylbenzenes. The similarity in temporal variability of these ion groups and their correspondence with NO$_x$ and alkylbenzene variation suggests these ion groups represent species emitted in roadway exhaust. We note that aldehydes such as heptanal and octanal may yield fragment ions at m/z 97 and 111 and perhaps produce the diel pattern evident in Figure 4.16. This type of sampling interference may be problematic for measuring cycloalkanes.

4.4.3.4. Naphthalenes and Naphthenic Monoaromatics

The other ions measured by PTR-MS were m/z 143 and 161. The m/z 143 ion corresponds to methylnaphthalene while the m/z 161 ion was a dominant signal in the diesel fuel mass spectrum but not abundant in gasoline and is attributed to a naphthenic monoaromatic
Figure 4.17 displays the time series for these ions. Compared to the alkanes and cycloalkanes, the \( m/z \) 161 response was small and hard to quantify. The first half of IVOC measurement was during a relatively clean period and the \( m/z \) 143 ion was not above detection limits but it displayed a significant response during the latter half when increased pollution was observed. Its temporal variability suggests that it is not methylnaphthalene from vehicle exhaust but rather a photooxidation product. If the response at \( m/z \) 143 was methylnaphthalene its variation would be expected to track IVOC alkanes. The \( m/z \) 143 ion signal intensity follows the daily variation of the photoproducts \( \text{NO}_2 \) (\( \text{NO}_y - \text{NO}_x \)) and \( \text{HCHO} \) with distinct daytime maxima and early morning minima as shown in the figure. This ion may be due to nonanal which could be created through ozone reactions with organics adsorbed onto inlet line surfaces (McClenny et al., 1998).

4.4.4. Tracer Comparison / Pollution Episodes

A number of measurements were deployed that can assist in the interpretation of the IVOC dataset (Figure 4.18). Since the primary influence on IVOC signal is attributed to diesel exhaust, comparing the IVOC alkane concentrations to other diesel constituents is a way to validate our interpretation of the IVOC data. The alkanes concentrations follow similar trends as the soot, CO, \( \text{NO}_x \), and alkylbenzenes. All of these species are constituents of both gasoline and diesel exhaust; soot concentrations are much more prominent in diesel compared to gasoline engine exhaust, while CO emissions are dominated by gasoline engines. The alkane concentrations were fairly low during extended periods of time, so to better define relationships between engine exhaust tracers, the comparison focussed on pollution episodes. PE 17 and PE 20 resulted in large increases in alkane mixing ratios and have a number of other measurements
for comparison. The largest concentrations of alkanes occurred on the 28th, but there was no available soot or AMS organics data, so the comparison was limited to PE 17 and PE 20.

4.4.4.1. PE 17

Figure 4.19 explores the relationship between different species during PE 17 occurring from Wednesday June 16th at approximately 20:00 through Thursday June 17th at 2:00. The alkanes reached nearly 2.5 ppbv along with increases in NO\textsubscript{x}, NO\textsubscript{y}, soot, CO, and toluene. The high levels of NO\textsubscript{x} also resulted in complete titration of O\textsubscript{3}. Given that there are only a few points, the correlations are good between the alkanes and diesel exhaust tracers. The soot (r\textsuperscript{2} = 0.97), CO (r\textsuperscript{2} = 0.87), NO\textsubscript{x} (r\textsuperscript{2} = 0.63), toluene (r\textsuperscript{2} = 0.96), and AMS organics (r\textsuperscript{2} = 0.89) showed good correlation with the alkanes suggesting a similar source. While toluene is a large component of both gasoline and diesel exhaust, the soot and AMS organics are much more prominent in diesel exhaust suggesting that there are large diesel vehicle emissions during this period. The observed slopes represents the relative abundances of alkanes within exhaust.

The slope observed between the alkanes and toluene was 0.85, which means there was an alkane to toluene ratio of 1.18. It was reported earlier that Zielinska et al. (1996) observed alkane to toluene ratios of ~0.1 for spark ignition dominated and 0.61 for diesel dominated. The CARES ratio appears to be reasonable knowing that the IVOC sampler measures a much larger range of IVOC alkanes than Zielinska et al. Reported and is expected to be larger.

In order to compare the alkanes to the soot and AMS organics, the alkane mixing ratio needs to be transformed into a concentration. Assuming an average MW of 194 for the alkanes and an average mixing ratio of 2.24 ppbv observed during the peak of PE 17 results in an alkane concentration of ~19 µg m\textsuperscript{-3}. Comparing this to the average concentrations during the peak of PE 17 for soot (0.670 µg m\textsuperscript{-3}) and AMS organics (~4 µg m\textsuperscript{-3}) suggests that there is nearly 30 and
around 5 times more IVOC alkanes by mass than soot and AMS organics respectively. Since alkanes are shown to lead to SOA formation the high relative abundance of them in polluted environments have the potential to significantly affect particulate matter on a greater level than direct vehicle emissions.

4.4.4.2. PE 20

Figure 4.20 explores the relationship between different species during PE 20 occurring from Sunday June 20th at approximately 18:00 through Monday June 21st at 1:00. The alkanes reached around 2 ppbv with NO\textsubscript{x} reaching nearly 30 ppbv, soot peaking around 770 ng m\textsuperscript{-3}, CO increasing to over 300 ppbv above background, and toluene reaching levels around 5 ppbv. Like PE 17, there are only a few points for PE 20. The PE 20 correlations are lower, but still relatively good between the alkanes and diesel exhaust tracers: soot ($r^2 = 0.95$), CO ($r^2 = 0.67$), NO\textsubscript{x} ($r^2 = 0.73$), toluene ($r^2 = 0.85$), and AMS organics ($r^2 = 0.32$). However, the slopes are fairly different from those observed during PE 17, with the ratios to alkanes being lower in general.

The slope observed between alkanes and toluene was 0.46 which is just over half the slope observed during PE 17. This results in an alkane to toluene ratio of 2.17, which still compares well to what would be expected based ratios observed by Zielinska et al. (1996). If this plume is a result of vehicles emissions, the higher alkanes to toluene ratio points towards higher diesel exhaust contribution during PE 20 than PE 17.

The alkane concentration during the peak of PE 20 was 16.5 µg m\textsuperscript{-3}. Comparing this to the soot (~0.4 µg m\textsuperscript{-3}) and AMS organics (5 µg m\textsuperscript{-3}) suggests that there is around 40 times and ~3 times more IVOC alkanes by mass than soot and AMS organics respectively. These ratios are relatively similar to those observed during PE 17, with there being less soot, but more AMS
organics. As with PE 17, the data suggests that the high relative abundance of alkanes could be a significant source of SOA.

4.5. Conclusion

Presented here was observations during CARES utilizing a PTR-MS with two custom built sampling methods. The first method utilized a dehumidifier to remove water vapor and increase the instrument's sensitivity. The observed alkylbenzenes suggested large anthropogenic sources, with concentrations of toluene reaching over 2 ppbv during large pollution episodes. The source of these emissions was attributed to vehicle exhaust as the winds transported the plume over Interstate Highway 80. Significant photoproduct activity was also observed during this time with observed increases in formaldehyde ($m/z$ 31), acetaldehyde ($m/z$ 45), and other photoproducts ($m/z$ 71, 73). There also appeared to be heavy biogenic emissions that occurred on the 14th, with observed increases in isoprene and isoprene photoproducts.

This was also the first quantification of the total abundance of C$_{10}$-C$_{17}$ IVOC alkanes in an urban environment. This was accomplished through the use of a newly developed thermal desorption sampling technique coupled with a PTR-MS and measurement of alkane ion fragments at $m/z$ 57, 71, 85 and 99. This IVOC sampler also allows for discrimination against VOC compounds that would be positive interferences at these masses. The total C$_{10}$-C$_{17}$ alkane mixing ratios reached nearly 3 ppbv during a few large pollution events. On average, the alkane mixing ratios were approximately 40% lower than the total alkylbenzene ($m/z$ 79, 93, 107, 121) mixing ratios, which suggests a relatively large abundance in urban environments. The ratio of alkanes to alkylbenzenes ($m/z$ 93, 107, 121) compared reasonably well with previous studies considering the IVOC sampler quantifies a larger range of isomers than the compared methods. The pollution episodes of June 17 and June 20 shoed that the measured IVOC alkane abundance was
strongly correlated to soot concentration. The strong correlation with soot is evidence that the measured ions can be attributed to exhaust emissions of alkanes, in particular diesel engine exhaust which is the dominant source of soot emissions in urban areas. During the pollution events, alkane concentrations were 30 to 40 times the concentration of soot, and 3 to 5 times greater than organic aerosol mass concentrations. The measured IVOC alkane abundance implies a significant pool of reactive compounds, comparable to the abundance alkylbenzenes, and should be considered in SOA formation in urban air quality.
4.6. References


Jordan, C.E., Ziemann, P.J., Griffin, R.J., Lim Y.B., Atkinson R., Arey, J.: Modeling SOA formation from OH reactions with C\textsubscript{8}-C\textsubscript{17} n-alkanes, Atmos. Environ., 42, 8015-8026, 2008.


4.7. Tables and Figures

Figure 4.1: Google map of Sacramento, CA. The red dot is the location of the T0 site at American River College.
Figure 4.2: Temperature, pressure, relative humidity, wind speed, and wind direction observed during CARES. The wind direction at 0° and 360° is north.
Figure 4.3: Observed trends in CO, O$_3$, SO$_2$, and NO$_x$ during CARES.
Figure 4.4: Time-series of alkylbenzenes ($m/z$ 79, 93, 107, 121, 135) measured with the PTR-MS dehumidifier technique during CARES.
Figure 4.5: Correlation between alkylbenzenes (m/z 79, 107, 121, 135) to toluene (m/z 93) during CARES.
Figure 4.6: Time-series of formaldehyde, ozone and methylhydroperoxide (left) and the correlation between these with formaldehyde (right) measured with the PTR-MS dehumidifier technique during CARES.
Figure 4.7: Mixing ratios (ppbv) of select VOC species measured with the PTR-MS dehumidifier technique along with O₃ and CO mixing ratios during CARES. Dashed lines indicate pollution episodes discussed in the text.
Figure 4.8: Isoprene ($m/z$ 69, green), methacrolien and methyl vinyl ketone ($m/z$ 71, blue), formaldehyde ($m/z$ 31, grey), and C$_3$-benzenes ($m/z$ 121, red) before and after the increase in pollution observed on the night of the 16$^{th}$ during PE 17.
Figure 4.9: Isoprene ($m/z$ 69, green), methacrolien and methyl vinyl ketone ($m/z$ 71, blue), and formaldehyde ($m/z$ 31, grey) observed during the beginning of CARES observations. All the traces have diel pattern suggesting biogenic sources. The correlation of $m/z$ 31 to 71 (right) suggests that isoprene oxidation as the major source for these ions.
Figure 4.10: Mixing ratios of select VOC tracers measured with the PTR-MS dehumidifier technique and O₃ and CO mixing ratios during CARES. Dashed lines indicate pollution episodes discussed in the text.
Figure 4.11: Comparison of responses observed at m/z 93, 121, 135 during the VOC and IVOC modes. The dashed line has a slope of 1.
Figure 4.12: Time-series of alkane ion response measured with the IVOC sampler during CARES. NO\textsubscript{x} mixing ratios averaged over the 30 minute IVOC sampling period are also shown.
Figure 4.13: Isoprene (m/z 69, green), methacrolien and methyl vinyl ketone (m/z 71, blue), formaldehyde (m/z 31, grey), and IVOC m/z 71 area counts (blue circles) on June 14th. The m/z 31, 69, and 71 show a diel pattern, which is attributed to biogenic emissions of isoprene and associated oxidation. The IVOC m/z 71 does not follow the same pattern, with no response observed when the other species are at their peak. This is evidence the IVOC system is efficiently discriminating against m/z 71 photoproducts, eliminating their interference.
Figure 4.14: Total IVOC alkane concentration determined from the sum of \textit{m}/\textit{z} 57, 71, 85 and 99 ion signals (bottom panel) measured with the IVOC sampler compared to the total alkylbenzene concentration from the sum of \textit{m}/\textit{z} 79, 93, 107, and 121 ion signals (top panel) measured with the dehumidifier.
Figure 4.15: Alkane mixing ratios from the IVOC sampler compared to the sum of alkylbenzene mixing ratios (m/z 93, 107, 121) observed through the dehumidifier.
Figure 4.16: Time-series of cycloalkane ion response measured with the IVOC sampler during CARES. Shown in the middle panel are mixing ratios of C$_2$-alkylbenzenes (m/z 107) and C$_3$-alkylbenzenes (m/z 121) measured with the dehumidifier.
Figure 4.17: Time-series of $m/z$ 161 area counts (upper panel), ozone (red trace) and formaldehyde (green trace) mixing ratios are shown in the middle panel, $m/z$ 143 area counts (blue circles) and NO$_2$ (red squares) are shown in the lower panel.
Figure 4.18: Time-series of key measurements during CARES. Alkane mixing ratios were determined from the IVOC sampler and toluene concentrations were determined from the dehumidifier.
Figure 4.19: Time-series of key measurements during PE 17. Alkane mixing ratios were determined from the IVOC sampler and toluene concentrations were determined from the dehumidifier.
Figure 4.20: Time-series of key measurements during PE 20. Alkane mixing ratios were determined from the IVOC sampler and toluene concentrations were determined from the dehumidifier.
CHAPTER 5: IDENTIFICATION OF DIESEL EXHAUST COMPONENTS USING A PTR-MS

5.1. Introduction

There are many factors that affect the air quality in an urban environment, but one of the more prominent sources of pollution is motor vehicle emissions. The vehicle fleet is a mixture of gasoline and diesel powered vehicles, but gasoline powered vehicles constitute the bulk of vehicle miles travelled in urban areas. The emissions from vehicles can be a large source of pollutants harmful to human health (HEI, 2010), with a number of studies linking adverse health effects with proximity to roadways (Brunekreef et al., 1997; Dockery et al., 2005, Dockery and Smith, 2007; Peters et al., 2004). These exhausts will also transform both chemically and physically as they are aged to generate additional harmful pollutants. The highly transformed (aged) exhaust can look quite different from the un-aged (freshly emitted) exhaust, with varying particle size, distribution, and chemical composition. People will be exposed to un-aged and aged exhausts, complicating the potential health effects. Therefore, in order to assess the health effects it is important to understand the chemical constituents of both aged and un-aged exhausts.

A joint collaboration study was performed concerning cardiovascular health effects of roadway emissions. This entailed a series of chamber experiments from April 27th to May 9th in 2012 at the Lovelace Respiratory Research Institute (LRRI) in Albuquerque, NM. The study was inspired by previous work that looked at how variable engine-loadings of a diesel engine effected cardiopulmonary and immune responses in animal models (McDonald, et al., 2011). The purpose of the study was to characterize the gas and particulate matter composition of the chamber to better understand chemical exposures in future animal and human studies being conducted by the University of Washington’s Center for Clean Air Research.
The observation (McDonald unpublished results) is that the combination of diesel and gasoline exhaust increases the toxicity greater than a combination of their individual health effects. This may be a result of the gasoline species partitioning onto the diesel exhaust particles. Under typical urban environment particulate matter concentrations the gasoline exhaust is volatile enough that it will exist primarily in the gas phase. It is hypothesized that gasoline exhaust species partition onto particles when exposed to high particle loads, increasing the toxicity of the particles. Since particles are significant in diesel exhaust and typical urban fleets include a mixture of diesel and gasoline engines, scenarios with high particle loadings from diesel exhaust will allow for low volatility gasoline species to partition to the particulate phase. The PTR-MS, outfitted with the dehumidifier and IVOC sampler, was deployed to quantify concentrations of both VOCs and IVOCs within the chamber. This chapter reports the relative abundance of a number of organic compounds, estimates their fuel based emission rates, explores the effect of engine load on relative abundances, proposes a mechanism for identifying the gasoline and exhaust contributions to a complex mixture, and looks at potential SOA yields from exhaust IVOC species.

5.2. Experimental

5.2.1. Lovelace Respiratory Research Institute

LRRI is outfitted with a number of exposure chambers (1.5 m³) and use a diesel electric generator (5.5 kW Yanmar) and a gasoline engine mounted to a dynamometer (1996 model General Motors 4.3-L V-6) to create mixtures of gasoline and diesel exhaust. The engines were operated at low, typical, and high loads. For the diesel electric generator this corresponded to a power output of 1.5 kW for a low load, 4.5 kW for a typical load, and 5.5 kW for a high load. For the gasoline engine the load corresponded to 1% throttle and 600 RPM for a low load, 11%
throttle and 1123 RPM for a typical load, and 27% throttle and 1922 RPM for a high load. These engines were housed in a common room and the exhaust ducted to the exposure chamber room across the hallway. McDonald et al. (2004; 2007; 2011) reported additional details on the LRRI facility and engine emissions. The PTR-MS sampled gasoline, diesel, and mixtures of both exhausts under varying engine loads and dilutions. Table 5.1 is a summary of the experiments performed.

The exhausts were diluted with clean, dry air and the dilution amounts were determined by measuring the particle mass concentration being delivered to the chamber compared to the maximum particle concentration that could be delivered to that point from the engine (gasoline or diesel). Undiluted diesel and gasoline exhaust would result in 400 and 50 µg m\(^{-3}\) particle loading in the chamber respectively. The dilution of the exhaust is determined by the ratio of the observed particle loading to the undiluted particle loading.

\[
D_D = \frac{P_{LD}}{400 \text{ µg m}^{-3}} \quad (5.1)
\]

\[
D_G = \frac{P_{LG}}{50 \text{ µg m}^{-3}} \quad (5.2)
\]

Where \(D_D\) and \(D_G\) equal the amount of dilution for the diesel and gasoline exhaust respectively and \(P_{LD}\) and \(P_{LG}\) are the observed particle loadings in µg m\(^{-3}\) for diesel and gasoline exhaust respectively. For example, an observed particle loading of 200 µg m\(^{-3}\) for diesel exhaust would signify 50% dilution. Generating a mixture of the exhausts started with running gasoline exhaust through the chamber until the desired particle loading was observed. The gasoline particle loading \((P_{LG})\) was recorded and diesel exhaust was added to the chamber while maintaining the same dilution of gasoline exhaust. The diesel exhaust dilution was adjusted until the desired particle loading contribution from the diesel was observed. The diesel particle loading \((P_{LD})\) to the particle loading was the difference between the measured particle loading \((P_{lob})\) and the
gasoline exhaust particle loading \( (PL_G) \). The composition of the mixture is determined by the 
ratio of the diesel dilution \( (D_D) \) or the gasoline dilution \( (D_G) \) to the sum of the dilutions \( (D_D + D_G) \).

\[
C_D = \frac{D_D}{D_D + D_G} \tag{5.3}
\]

\[
C_G = \frac{D_G}{D_D + D_G} \tag{5.4}
\]

Where \( C_D \) and \( C_G \) are the percent of the mixture composed of diesel and gasoline exhaust 
respectively. For example, during experiment 2 \( PL_G \) was 12 \( \mu \text{g m}^{-3} \) and was \( PL_D \) 370 \( \mu \text{g m}^{-3} \).

Equations 5.1 and 5.2 would generate exhaust dilution of 0.24 for \( D_G \) and 0.93 for \( D_D \). Using 
these values in equations 5.3 and 5.4 would result in a mixture of 21% gasoline and 79% diesel 
exhaust. The calculated mixtures for each experiment are shown in Table 5.1.

5.2.2. Instrumentation

The PTR-MS was deployed along with the dehumidifier (section 4.3.2.1) and the IVOC 
sampler (section 2.2). By purging the Tenax trap before desorption, the light alkenes and other 
VOCs can be removed to make identification of IVOC alkanes and other species tractable.

Several desorption purge temperatures were tested to find the optimum temperature for VOC 
discrimination without significant loss of IVOC alkane species. A 150 °C purge temperature 
was chosen as this provided effective removal of interfering VOC compounds while limiting 
losses of \( \text{C}_{12} \) and larger alkanes. The method was shown to remove the interference from 
methacrolein \( (m/z \ 71) \), alkenes and alkanes < \( \text{C}_9 \), aldehydes < \( \text{C}_6 \), benzene, and toluene. The 
IVOC thermal desorption sampler effectively measures alkanes from the \( \text{C}_{10}-\text{C}_{18} \) range with the 
upper range limited by the ability to effectively transfer low volatility compounds through PTR-
MS sample lines and valves. Section 2.3.7 has further details on the IVOC sampler 
\ discrimination method.
The sensitivities of many IVOC species has to be estimated due to the lack of calibration standards. If the reaction of the species is expected to occur at the collisional rate, the theoretical and measured sensitivities can be used to estimate sensitivity at any given \( m/z \) value. The same methods for determining theoretical and measured sensitivities as detailed in section 2.1.3.4 were utilized. Table 5.2 shows the measured sensitivities from the calibration gas standard (Scott-Marrin) during the Lovelace experiments, along with the estimated sensitivities for the other ions. Figure 5.2 shows the theoretical, measured, and a ratio of the measured sensitivities to the theoretical sensitivities plotted versus \( m/z \). An exponential line was fit to each dataset and resulted in the following equations:

\[
\text{ncps}_{\text{measured}} = -6.1 + 33.6 \times e^{-0.0091 \times \left(\frac{m}{T}\right)} \\
\text{ncps}_{\text{theoretical}} = 33.6 - 27.5 \times e^{-0.0041 \times \left(\frac{m}{T}\right)} \\
\frac{\text{ncps}_{\text{measured}}}{\text{ncps}_{\text{theoretical}}} = -0.15 + 3.4 \times e^{-0.016 \times \left(\frac{m}{T}\right)}
\]

For a given \( m/z \), the sensitivity can be estimated by calculating the measured to theoretical ratio using equation 5.7 and multiplying it by the theoretical sensitivity. Table 5.2 lists the sensitivities used at the different ions for calculating IVOC mixing ratios and are identified by bold type font in the estimated ncps column. The listed species were used in the generation of equations 5.5 to 5.7. If there is not sufficient knowledge of the species to calculate a theoretical sensitivity, equation 5.6 can be used to estimate the value assuming the collisional rate of the species is similar to the surrounding ions. These sensitivities were then translated into area counts nmol\(^{-1}\) as described in section 2.3.3. To determine the alkane mixing ratios, the response at \( m/z \) 57, 71, 85, 99, and 113 were summed and a sensitivity of \(8.01 \times 10^4\) AC nmol\(^{-1}\) was used. This sensitivity was determined from calibrations with diesel fuel and is further detailed in section 3.3.5.
5.3. Results

5.3.1. Vehicle Exhaust Composition

Figure 5.3 shows the composition of diesel exhaust and gasoline exhaust as observed with the dehumidifier and the IVOC sampler under the 150 °C purge scenario. The colors represent ions that have a similar molecular structure and have been reported to be components of vehicle exhausts (Hoekman, 1992; Schauer et al., 1999, Schmitz et al., 2000; Schauer et al., 2002; Smith et al., 2002; Jobson et al., 2005) and have been identified as important compound groups within vehicle exhaust in sections 3.3.2 and 3.3.3. The exhaust composition was determined by applying the estimated sensitivities from Table 5.2 to the PTR-MS measured response, resulting in the mixing ratios of selected species displayed in Figure 5.3. The engines were operated at a typical load, but the diesel exhaust was diluted by 25% and the gasoline exhaust was diluted by 60%. The VOC mode alkane and alkene response is largely attributed to the response of alkenes, along with the some fragmentation from larger species. Since the IVOC alkane mixing ratios were calculated from the sum of the IVOC response at \( m/z \) 57, 71, 85, 99, and 113, the mixing ratios are shown as a different category.

The relative abundance of species observed in VOC mode is very similar, with the highest signal observed in the alkylbenzenes \( (m/z \) 79, 93, 107, 121, 135), alkenes and alkanes \( (m/z \) 43, 57, 71, 85), and the oxygenated species \( (m/z \) 31, 45, 59). The cycloalkanes \( (m/z \) 83, 97, 111, 125, 139), bicycloalkanes \( (m/z \) 81, 95, 109, 123, 137, 151, 165, 179), naphthenic monoaromatics \( (m/z \) 105, 119, 133, 147, 161, 175), and naphthalene \( (m/z \) 129, 143, 157) are not as prominent, but present within both exhausts. The observations in IVOC mode show clear differences between the diesel and gasoline exhausts. The biggest changes in IVOC mode is the discrimination against VOC species, with species like benzene \( (m/z \) 79) and toluene \( (m/z \) 93)
decreasing by a factor of ~100. In general, the diesel exhaust sees the same relative decrease at most ions as the gasoline, except for the heavier masses. There is a more prominent signal at \( m/z \) 157, 161, 163, 165, 175, and 179. This is attributed to the higher abundance of IVOC species within the diesel exhaust compared to gasoline. Table 5.3 compares the percentage of ion abundance for selected ions in VOC and IVOC within the different compound groups for the exhausts. VOC mode observations show that both exhausts are dominated by alkylbenzenes, alkenes and alkanes, and oxygenated species. This distribution is shifted slightly in the IVOC mode, resulting in some differences between the exhausts. The IVOC alkanes and alkylbenzenes have a comparable composition within the diesel exhaust while the gasoline exhaust is dominated by IVOC alkylbenzenes.

The IVOC alkane mixing ratios were 145 ppbv and 100 ppbv within the diesel and gasoline exhaust respectively. These are relatively similar, but they do not account for the differences in dilution. Looking at the C\(_{1}\)-C\(_{3}\) VOC alkylbenzene concentrations, large differences in the abundances can be observed with mixing ratios of 556 ppbv seen in the diesel exhaust and ~3800 ppbv seen in the gasoline exhaust. Taking the ratio of alkanes to the VOC alkylbenzenes (\( m/z \) 93, 107, 121) results in values of 0.26 and 0.026 for diesel and gasoline exhaust respectively. It was stated in section 3.3.6 that Schauer et al. (1999) saw a molar ratio of 0.2 within diesel exhaust, which is close to the ratio of 0.26 observed by the IVOC sampler. The higher ratio may be attributed to the C\(_{12}\)-C\(_{18}\) branched alkanes that are observed by the IVOC sampler but not reported by Schauer et al. (1999). Calculating the same molar ratio for gasoline exhaust from data reported by Schauer et al. (2002) resulted in a molar ratio of ~0.002, which is significantly lower than the ratio of 0.026 observed by the IVOC sampler. A small portion of this difference may be due to the inclusion of branched alkanes in the IVOC sampler ratio that
were not reported by Schauer et al. (2002), but it would not be expected to account for the factor of 10 difference. It is unclear the cause of this large difference and requires further investigation. While the IVOC alkanes are the most abundant, some of the other species have a large presence in both exhausts. In diesel exhaust, the naphthenic monoaromatics ($m/z$ 133, 147, 161, 175) reached 57 ppbv, the naphthalenes ($m/z$ 129, 143, 157) reached 47 ppbv, and the bicycloalkanes ($m/z$ 137, 151, 165, 179) reached 26 ppbv. The sum of these groups resulted in 129 ppbv, which is comparable to the 145 ppbv of IVOC alkanes. This suggests that these other IVOC species could play as significant a role in urban air quality as the IVOC alkanes. In gasoline exhaust, the mixing ratios of naphthenic monoaromatics were 57 ppbv, naphthalenes were 46 ppbv, and bicycloalkanes were 10 ppbv, which summed up to a mixing ratio of 112 ppbv. These groups are also present in comparable abundances to the IVOC alkanes (100 ppbv) within gasoline exhaust.

5.3.2. Vehicle Exhaust Emission Ratios

Since the exhausts were measured under different dilutions, the mixing ratios (ppbv) were normalized to the $\Delta$CO$_2$ mixing ratio (ppmv) to allow for better comparison between the experiments. Since CO$_2$ mixing ratios are well characterized in vehicle emissions, this allows for an estimation of fuel based emission rates and help assess their relative contribution to urban air pollution. The dilution gas contained atmospheric background levels of CO$_2$ (assumed to be 380 ppmv), so the $\Delta$CO$_2$ refers to the measured background corrected observed CO$_2$ mixing ratios. To measure CO$_2$ mixing ratios, a LI-840 CO$_2$/H$_2$O analyzer from LI-COR was utilized. The instrument is designed with automatic temperature and pressure corrections and a measurement range up to 20,000 ppm with an accuracy within 1% of the reading. The noise is less than 1 ppm around typical atmospheric concentrations and has a minimal zero and span drift.
The IVOC-to-ΔCO$_2$ molar ratios (emission ratios) for both exhausts are displayed in Figure 5.4. The emission ratios are very similar for the smaller ions associated with the alkylbenzenes, bicycloalkanes, naphthenic monoaromatics, and naphthalenes. The highest emission rates for both exhausts were observed for the C$_2$- and C$_3$-alkylbenzenes ($m/z$ 121, 135) and alkanes. Table 5.4 is a summary of the emission ratios observed in IVOC mode for key IVOC exhaust species. The alkylbenzene ratios were quite similar, but the diesel exhaust IVOC alkane emission ratio was approximately 3.5 times greater than gasoline engine exhaust. The diesel exhaust total VOC alkylbenzene emission ratio was about 40% lower than in gasoline exhaust. The IVOC alkane emission ratios were about 5 times lower than VOC alkylbenzenes in diesel exhaust and 25 times lower in gasoline exhaust. The total IVOC emission ratio was determined by summing up the cycloalkanes, bicycloalkanes, naphthenic monoaromatics, naphthalenes and alkanes. This resulted in a total IVOC emission ratio of ~0.28 for diesel exhaust, which is about 3 times higher than the emission ratio of ~0.1 observed in gasoline exhaust.

There are also vast differences at the higher ions, with $m/z$ 165, 175, and 179 emission ratios being approximately 46, 22, and 54 times higher respectively in the diesel than gasoline. These ions are part of the naphthenic monoaromatics and bicycloalkanes, with emission ratios approximately 4 and 10 times lower respectively than the alkanes. Combined, the emission ratios for these groups approximately 35% the magnitude of the alkane ratios, suggesting that these species could be as important SOA precursors as alkanes.

What the emissions ratios don’t account for is the composition of the vehicle fleet. The California State Board of Equalization reports the monthly gallons of gasoline and diesel fuel sold (http://www.boe.ca.gov/sptaxprog/spftrpts.htm). Utilizing the data from 2012, there was
approximately 14.6 and 2.6 billion gallons of gasoline and diesel fuel sold respectively. From this, we estimate fleet emissions to be composed 85% gasoline and 15% diesel vehicle emissions. The Environmental Protection Agency reported that gasoline and diesel engines emit comparable amounts of CO$_2$ per unit of burned fuel: 8,887 and 10,180 grams CO$_2$ gallon$^{-1}$ respectively (EPA, 2011). This can be translated to 202 and 231 moles CO$_2$ emitted per gallon for gasoline and diesel vehicles respectively. Using this information, the emissions from a typical vehicle fleet can be estimated. The emission ratios listed in Table 5.4 can be expressed as moles m/z per 1000 moles CO$_2$, which can then be multiplied by the CO$_2$ molar emissions per gallon to estimate the moles of IVOCs emitted per gallon of fuel consumed. This results in IVOC molar emission rates of 0.019 and 0.065 moles gallon$^{-1}$ for gasoline and diesel vehicles respectively and are shown in Table 5.5. The diesel vehicle IVOC molar emissions are approximately 3.4 times higher than the gasoline IVOC molar emissions. The molar emissions can then be normalized to the vehicle fleet composition by multiplying the gasoline molar emissions by 0.85 and the diesel molar emissions by 0.15, resulting in IVOC molar emissions of 0.016 and 0.01 for gasoline and diesel vehicles respectively. This is an interesting result suggesting that the gasoline vehicles emit a similar magnitude of IVOCs as the diesel vehicles. Comparison of the total IVOC molar emissions to the VOC alkylbenzene (m/z 79, 93, 107, 121, 135) emissions, there are approximately 18 times more VOC alkylbenzenes moles emitted from a typical vehicle fleet than IVOCs. An important thing to note is the gasoline emissions were from a 1996 model year engine. Gasoline emissions have decreased significantly over the last two decades, so the information presented here is likely an overestimation of gasoline vehicle contribution.
5.3.3. Role of Engine Load on Relative Abundances

The previous discussion of emission ratios only pertains to the engines under a typical load. It is also important to note how the emission ratios change under different loads. Figure 5.5 shows the emission ratio profile for diesel and gasoline under different engine loads as observed with the VOC and IVOC modes. As observed before, the diesel and gasoline exhaust look similar in the VOC mode. The gasoline typical and low loads have the overall highest emission ratios relative to CO$_2$, with the diesel typical load showing similar emission ratios for most ions and the diesel low load being slightly lower, but following the same trend. The diesel engine high load did not have the same trend as the other engine load profiles. The diesel high load was more dilute, with a lower particle loading (72 µg m$^{-3}$) compared to the diesel typical (288 µg m$^{-3}$) and diesel low load (292 µg m$^{-3}$) experiments, but it is not clear if this is the cause and requires further investigation. During the high engine load gasoline exhaust sampling experiment, the IVOC mode response for many species was below or near the detection limit, so it is not included in this analysis.

The IVOC mode emission ratios were quite different from the VOC mode. The highest emission ratios were generally observed with the diesel typical load. The gasoline typical and low loads showed similar ratios as the diesel typical load for the alkylbenzenes, light bicycloalkanes, and light naphthenic monoaromatics. The diesel low load has comparable emission ratios to the gasoline typical and low loads, except it does not have as prominent of a response of alkylbenzenes, light cycloalkanes, and light naphthenic aromatics. The lowest emission ratios were observed with the diesel high load. The major difference between diesel and gasoline exhaust is observed at the higher ions ($m/z$ 161, 165, 175, 179). At these ions, no
matter the load, the gasoline emission ratios are lower than observed in the diesel typical and low loads.

5.3.4. Vehicle Exhaust Signatures

While normalizing the exhaust to CO$_2$ provides valuable information, there are many CO$_2$ sources in an urban environment that would skew this relationship, making it hard to use this ratio as a vehicle exhaust signature. The exhaust was normalized to the C$_4$-benzenes ($m/z$ 135) due to their large abundance in gasoline and diesel exhaust. The observed IVOC mixing ratios for both exhausts and all loads were normalized to $m/z$ 135 resulting in the abundance ratios shown in Figure 5.6. In general, the gasoline abundance ratios are lower than the diesel abundance ratios, except under the high engine load. As stated previously, the high engine load gasoline exhaust sampling experiment was not included due to many species being near the detection limit.

The abundance ratios can provide useful information on urban sources of organic compounds. For compounds with abundance ratios that are the same in both gasoline and diesel exhaust, deviations from this ratio in urban air would suggest non-vehicle sources. If vehicle emissions are the dominant source, the abundance ratio profiles for each engine exhaust type can also potentially be used as source signatures to quantify the relative contributions of diesel and gasoline engine exhausts to organic compound concentrations in urban air. For this study, it was found that a mixture containing diesel and gasoline engine exhaust yielded compound abundance ratios between the two pure exhaust source ratios as shown in Figure 5.7. Section 3.3.6 presented two equations for estimated the observed exhaust mixture ratios with equation 3.3 and 3.4.

$$ R_i = (x \times D_i) + (y \times G_i) $$

$$ x + y = 1 $$
Some of the estimated mixtures from Table 5.1 were applied to equation 3.3 with the associated diesel and gasoline abundance ratios to estimate the exhaust ratios. These estimations were then compared to the observed ratios to test the fidelity of this method. Figure 5.7 shows the estimated ratios compared to the observed ratios for a mixture of 89% gasoline exhaust and 11% diesel exhaust during experiment 8. The estimated ratios follow fairly closely to the observed ratios, except there is overestimation where the lowest gasoline ratios are observed at $m/z$ 139, 165, 175, and 179. As detailed in section 5.3.2, a typical vehicle fleet was estimated to be 85% gasoline vehicles and 15% diesel vehicles. This means the experiment 8 ratios are close to what would be observed in a typical urban environment.

To test the fidelity of this method, the observed ratio was plotted versus the estimated ratio and compared to a one to one line. The results are shown in Figure 5.8. In general, the best estimations occurred under higher particle loads, typical engine loads, and a mixture with at least 40% gasoline (experiments 4, 8, and 9). Experiment 5 showed the most variability between the observed and estimated with there being a general underestimation of the ratios. This experiment also saw the lowest particle load (4 µg m$^{-3}$), which means both exhausts were highly diluted. It would suggest that the ratio estimation method does not work well for highly diluted mixtures or the mixing scheme does not perform as well at this high dilution level. There was also underestimation of the ratios during experiments 2 and 17. This may be a result of a higher composition of diesel exhaust than gasoline (>50%) and/or a high particle load (>300 µg m$^{-3}$). However, experiment 15 was mostly composed of diesel exhaust (78%), but had a much lower particle load (118 µg m$^{-3}$), but the estimated ratios agreed fairly well with the observed ratios. This would suggest that the ratio estimation method does not work well for high particle loads or the mixing scheme does not perform as well at high particle loads.
(>300 µg m\(^{-3}\)). Overall, the ratio estimation method appears to work well under most conditions except when the mixture is highly diluted or there are high particle loads.

5.3.5. Diesel Exhaust SOA Formation

Several studies have shown the importance of SOA formation from IVOC species (Robinson et al., 2007; Shirvastava et al., 2008). By photochemically aging diesel exhaust in a chamber, Robinson et al. (2007) reported that at most 15% of the SOA formation could be accounted for by traditional SOA precursors and hypothesize that the remaining 85% of SOA formation is from IVOCs. In their study, 90% of the traditional SOA formation was due to light alkylbenzenes (\(m/z\) 79, 93, 107, 121). The IVOC sampler and dehumidifier exhaust sampling provide a good dataset for testing Robinson’s hypothesis, which suggests at least 5.7 times more SOA formation from IVOCs than the VOC alkylbenzenes. This will be done by estimating the SOA formation from the IVOC species and light alkylbenzenes and comparing the ratio of IVOC to VOC SOA formation to Robinson et al. (2007).

The SOA formation was estimated from an equation utilized by Chan et al. (2009):

\[
M_{SOA,i} = M_{HC,i}(1 - e^{-k_{OH,i}[OH] \Delta t}) \times Y_i
\]  

For a given species \(i\), \(M_{SOA,i}\) is the SOA formation (g gallon\(^{-1}\)), \(M_{HC,i}\) is the mass emission (g gallon\(^{-1}\)), \(k_{OH,i}\) is the OH reaction rate constant, \([OH]\) is the concentration of OH, \(\Delta t\) is the reaction time, and \(Y_i\) is the SOA yield. The reaction time \(\Delta t\) was assumed to be 3 hours, which is how long Robinson et al. (2007) photochemically aged the diesel exhaust. Robinson et al. (2007) assumed an OH concentration of 2x10\(^{-6}\) molecules cm\(^{-3}\), so this value was used in our calculations. The OH reaction rates were estimated from Atkinson and Arey (2003) and Phousongphouang and Arey (2002) and are listed in Table 5.6. The SOA yields are expressed as the ratio of SOA mass formed to mass of species reacted and were estimated from a number of
sources. Chan et al. (2009) explored the SOA yields of naphthanlene, 1-methylnaphthalene, and 2-methylnaphthalene over a series of chamber experiments and reported SOA yields of 0.26, 0.36, and 0.31 respectively. These yields were also used to estimate the SOA yields of the bicycloalkanes and naphthenic monoaromatics. Lim et al. (2005) explored the SOA yields of C_8–C_{15} n-alkanes with a series of chamber tests. The SOA yields reported are low for octane (C_8) (~0.005), but increase rapidly to ~0.5 for tridecane (C_{13}) where the SOA yields appear to level off for the larger alkanes. Since most of the alkanes measured by the IVOC sampler are C_{13} and larger, an SOA yield of 0.50 was assumed. The SOA yields for alkylbenzenes have been explored by Ng et al. (2007) and Odum et al. (1996). Taking average SOA yields from the chamber experiments reported by Odum et al. (1996) results in an SOA yields for m-xylene and 1,2,4-trimethylbenzene as 0.0375 and 0.046 respectively. Ng et al. (2007) reported SOA yields of 0.19 and 0.1 for benzene and toluene respectively. An SOA yield of 0.1 was assumed for all C_{10} and larger alkylbenzenes.

Table 5.6 shows the estimated SOA formation from the IVOCs and VOC alkylbenzenes in diesel exhaust. The emission rates in grams per gallon of fuel consumed were calculated from the molar emissions of each species. These mass emissions were used in equation 5.6 to get a estimate of SOA mass per gallon of fuel consumed. The sum of SOA formation from IVOC diesel exhaust species was 9.4 g gallon^{-1}. Comparing this to the 1.5 g gallon^{-1} of SOA formed from VOC alkylbenzenes (m/z 79, 93, 107, 121) results in an IVOC to VOC SOA ratio of 6.37. This value supports the hypothesis of Robinson et al. (2007) that most of the SOA formation from diesel exhaust is from IVOC precursors. The IVOC alkanes showed the highest SOA formation and accounted for approximately 60% of the SOA. The naphthenic monoaromatics
and bicycloalkanes accounted 20% of the SOA formation, suggesting they play an important role in urban SOA formation.

5.4. Conclusion

The PTR-MS and IVOC sampler was deployed to the Lovelace Respiratory Research Institute to study vehicle exhausts through series of chamber experiments. Observations in IVOC and VOC mode of gasoline and diesel exhaust showed that they are very similar in composition, the exception being that diesel exhaust has a higher relative abundance of heavier organics. Normalizing the observed mixing ratios to $\Delta$CO$_2$ resulted in emission ratios for the different IVOC species. These emission ratios can help assess the relative emissions of IVOC species and may serve to estimate their emissions in the atmosphere. It was found that the emission of IVOCs is 2.9 times greater in diesel exhaust than gasoline and that the summation of bicycloalkanes and naphthenic monoaromatics is comparable to that for IVOC alkanes. Estimation of the emissions of a typical vehicle fleet resulted in VOC alkylbenzene emissions being approximately 18 times greater than IVOC emissions.

Observations of different engine loads showed that the lowest IVOC emission ratios were observed under the high engine loads and the highest emission ratios were observed with the diesel exhaust typical engine load. The gasoline typical and low loads showed comparable emission ratios to the diesel typical load for some of the lighter organics. Normalizing the IVOC mixing ratios to $m/z$ 135 introduced a metric that can determine the relative contribution of gasoline and diesel exhaust to a mixture. This was done by observing the differences in observed abundance ratios. The estimated ratios were similar to the observed ratios except when there was high dilution or a high particle load (>300 $\mu$g m$^{-3}$). Investigation of SOA formation from IVOC species in diesel exhaust supported the hypothesis of Robinson et al. (2007)
suggesting that SOA formation from IVOCs is more than a factor of 5.7 higher than VOC alkylbenzene SOA formation. This suggests that the IVOC species will play an important role in urban SOA formation.
5.5. References


### 5.6. Tables and Figures

Table 5.1: Summary of experiments performed at LRRI. The IVOC column refers to the number of peaks sampled using the specified purge temperature (°C). Ch = Chamber number. D = diesel exhaust. G = gasoline exhaust. UW = University of Washington sampling. SMPS = Scanning Mobility Particle Sizer sampling. VOC = PTR-MS dehumidifier sampling. T = typical engine load. L = low engine load. H = high engine load.

<table>
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<th>Start Time</th>
<th>Ch</th>
<th>Particle Loading (µg m&lt;sup&gt;-3&lt;/sup&gt;)</th>
<th>Engine Load</th>
<th>Estimated Dilution (%)</th>
<th>Estimated Mixture (%)</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>UW</th>
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Table 5.2: Measured, theoretical, and estimated PTR-MS sensitivities utilized for IVOC mode mixing ratio calculations. The sensitivities used are in bold type font. The species used to estimate the sensitivity are listed in the species column.

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Table 5.3: Percent of total organic ion signal of key ion groups in diesel and gasoline exhaust for typical engine loads observed with the dehumidifier and IVOC sampler.

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Table 5.4: Emission ratios of key exhaust species relative to CO$_2$ (m/z ppbv / CO$_2$ ppmv).

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Table 5.5: Estimated IVOC emission rates per gallon of fuel consumed for a typical vehicle fleet.

<table>
<thead>
<tr>
<th></th>
<th>Gasoline</th>
<th>Diesel</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>grams CO$_2$ per gallon</td>
<td>8887</td>
<td>10180</td>
<td></td>
</tr>
<tr>
<td>moles CO$_2$ per gallon</td>
<td>202</td>
<td>231</td>
<td></td>
</tr>
<tr>
<td>2012 CA Fuel Sales (billions of gallons)</td>
<td>14.6</td>
<td>2.6</td>
<td>17.2</td>
</tr>
<tr>
<td>% Total Sales</td>
<td>85</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Emissions (moles / 1000 moles CO$_2$)</td>
<td>IVOC</td>
<td>0.096</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>VOC alkylbenzenes</td>
<td>2.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Emissions (moles / gallon)</td>
<td>IVOC</td>
<td>0.019</td>
<td>0.065</td>
</tr>
<tr>
<td></td>
<td>VOC alkylbenzenes</td>
<td>0.49</td>
<td>0.32</td>
</tr>
<tr>
<td>Typical Fleet Emissions</td>
<td>IVOC</td>
<td>0.016</td>
<td>0.010</td>
</tr>
<tr>
<td>(moles / gallon of total fuel)</td>
<td>VOC alkylbenzenes</td>
<td>0.42</td>
<td>0.049</td>
</tr>
</tbody>
</table>
Table 5.6: Estimated mass of SOA formed from IVOCs and VOC alkylbenzenes in diesel exhaust.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Emission (ppbv / ppmv CO₂)</th>
<th>Mass Emission (grams / gallon)</th>
<th>SOA Yield</th>
<th>kOH</th>
<th>SOA (grams / gallon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bicycloalkanes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>151</td>
<td>0.0055</td>
<td>0.82</td>
<td>0.31</td>
<td>6E-11</td>
<td>0.18</td>
</tr>
<tr>
<td>165</td>
<td>0.0042</td>
<td>0.70</td>
<td>0.31</td>
<td>6E-11</td>
<td>0.16</td>
</tr>
<tr>
<td>179</td>
<td>0.0056</td>
<td>0.99</td>
<td>0.31</td>
<td>6E-11</td>
<td>0.22</td>
</tr>
<tr>
<td>Alkylbenzenes (IVOC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>135</td>
<td>0.11</td>
<td>15</td>
<td>0.1</td>
<td>9.5E-12</td>
<td>0.28</td>
</tr>
<tr>
<td>149</td>
<td>0.021</td>
<td>3.1</td>
<td>0.1</td>
<td>5.65E-11</td>
<td>0.22</td>
</tr>
<tr>
<td>163</td>
<td>0.012</td>
<td>2.0</td>
<td>0.1</td>
<td>1.13E-10</td>
<td>0.18</td>
</tr>
<tr>
<td>Naphthenic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monoaromatics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>147</td>
<td>0.015</td>
<td>2.2</td>
<td>0.355</td>
<td>4.48E-11</td>
<td>0.49</td>
</tr>
<tr>
<td>161</td>
<td>0.011</td>
<td>1.8</td>
<td>0.31</td>
<td>6E-11</td>
<td>0.40</td>
</tr>
<tr>
<td>175</td>
<td>0.011</td>
<td>2.0</td>
<td>0.31</td>
<td>6E-11</td>
<td>0.44</td>
</tr>
<tr>
<td>Naphthalenes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>129</td>
<td>0.014</td>
<td>1.8</td>
<td>0.26</td>
<td>2.3E-11</td>
<td>0.18</td>
</tr>
<tr>
<td>143</td>
<td>0.015</td>
<td>2.2</td>
<td>0.355</td>
<td>4.48E-11</td>
<td>0.48</td>
</tr>
<tr>
<td>157</td>
<td>0.013</td>
<td>2.1</td>
<td>0.31</td>
<td>6E-11</td>
<td>0.47</td>
</tr>
<tr>
<td>Alkanes</td>
<td>57, 71, 85, 99, 113</td>
<td>0.15</td>
<td>31.9</td>
<td>0.5</td>
<td>2.07E-11</td>
</tr>
<tr>
<td>Total IVOC Emission Ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.39</td>
<td>67</td>
<td></td>
<td></td>
<td>9.4</td>
</tr>
<tr>
<td>Alkylbenzenes (VOC)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>0.25</td>
<td>19</td>
<td>0.19</td>
<td>1.22E-12</td>
<td>0.10</td>
</tr>
<tr>
<td>93</td>
<td>0.34</td>
<td>31</td>
<td>0.1</td>
<td>5.63E-12</td>
<td>0.36</td>
</tr>
<tr>
<td>107</td>
<td>0.41</td>
<td>44</td>
<td>0.0375</td>
<td>1.45E-11</td>
<td>0.44</td>
</tr>
<tr>
<td>121</td>
<td>0.28</td>
<td>34</td>
<td>0.0463</td>
<td>2.20E-11</td>
<td>0.59</td>
</tr>
<tr>
<td>sum</td>
<td>1.3</td>
<td>128</td>
<td></td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>IVOC:VOC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.31</td>
<td>0.52</td>
<td></td>
<td></td>
<td>6.37</td>
</tr>
</tbody>
</table>

Figure 5.1: Plumbing schematic showing thermal desorption sampler for IVOC compounds and VOC sampling system with water vapor trap.
Figure 5.2: Measured and theoretical PTR-MS sensitivities along with a plot of the ratio between the two.
Figure 5.3: Mixing ratios of key ions within diesel and gasoline exhaust observed with the dehumidifier and IVOC sampler. Alks represents the alkane mixing ratios determined from IVOC mode.
Figure 5.4: IVOC emission ratios of diesel and gasoline exhaust. Alks represents the alkane mixing ratios determined from IVOC mode.
Figure 5.5: Emission ratios of key ions within diesel and gasoline exhaust under different engine loads.
Figure 5.6: Relative abundance to $m/z$ 135 of key ions within diesel and gasoline exhaust observed with the IVOC sampler.
Figure 5.7: Vehicle signature for diesel and gasoline exhaust under typical engine loads compared to two mixtures of both exhausts.
Figure 5.8: Comparison of the observed exhaust ratios to the estimated exhaust ratios for variable mixtures of gasoline and diesel exhaust. The solid black line has a slope of 1. The experiment # corresponds to the experiment listed in Table 5.1.
CHAPTER 6: THE NEED AND STEPS TOWARDS CREATING A GREENHOUSE GAS INFORMATION SYSTEM

6.1. Introduction

Improving our ability to understand the sources and sinks of greenhouse gases (GHGs) such as carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), hydrofluorocarbons (HFCs), perfluorinated hydrocarbons (PFCs), and sulfur hexafluoride (SF$_6$) is critical to understanding climate change. In order to evaluate the effectiveness of policies to mitigate the adverse impacts of climate change we need to increase our knowledge of the causes and consequences. There is already a large network of GHG observations, modeling, and information synthesis in the US that aid in our understanding of GHG and their role in climate change. Monitoring networks (e.g. AmeriFlux) provide continuous observations of GHGs. Models provide climate projections, and ongoing research has increased our knowledge of GHG environmental interactions.

While the physical effect of these gases in warming the atmosphere is well understood, there are still large knowledge gaps concerning estimating, monitoring, and modeling emissions and ambient GHG concentrations. There are also gaps in our ability to integrate this understanding to address scientific and policy questions in a comprehensive way. Part of this is due to a lack of connectivity across the diverse greenhouse gas research and measurement communities.

The gaps associated with GHG research can be summarized into three general categories: operational, scientific knowledge, and coordination. The operational gaps are associated with integration of new technology, the standardization of data handling, calibration, validation, and verification of current observation and modeling techniques. The large variety of observation practices and data handling introduces challenges in integrating the information. The scientific
knowledge gaps are associated with observations, models, process understanding, and
development of new technology and methods. Although there are ongoing improvements and
innovations, this can often be disjointed. The coordination gaps are associated with
collaboration between groups and agencies and the translation of information to external groups
(public, policy makers, agencies, etc.).

A few recent reports (Michalak et al., 2011; Pacala et al., 2010; Dimotakes et al., 2011)
have called for a centralized greenhouse gas information system (GHGIS) as a focal organization
for addressing a number of these issues. Such a system would take on the task of closing the gaps
and increasing our integrated national GHG monitoring capabilities. This would generate better
understanding of GHG effects, better policy making, and better metrics by which to evaluate the
feasibility and success of proposed and implemented policies. There are a few overarching
characteristics that a GHGIS should have in order to be effective. These include increasing the
ability to maintain long-term observations, improving modeling skill and data handling,
strengthening links between organizations concerned with GHG effects, guide the development
of new technology and practices, and facilitate the transfer of knowledge concerning GHGs to
the appropriate entities (public, policy makers, etc.) (Michalak et al., 2011; Pacala et al., 2010;
Dimotakes et al., 2011). An integrated system will help increase scientific knowledge, allow
better quantification of climate changes and their effects, aid in mitigation and adaptation
strategies, and help maintaining compliance with regulations. This chapter explores the need to
progress towards a national GHGIS.

6.2. GHGIS Capabilities

Taking current structure of GHG research and combining this with solutions for filling
the gaps, the basic characteristics of a GHGIS can be identified. The organization should work
to expand and maintain the current observation capabilities. Current observing networks include in situ measurements and remote sensing. The FluxNet and AmeriFlux networks are composed of micrometeorological towers and measure CO$_2$ using the eddy covariance method. The Department of Energy Atmospheric Radiation Measurement program has a number of permanent and mobile facilities that measure CO$_2$ concentrations and/or fluxes. The National Oceanic and Atmospheric Administration Office of Marine and Aviation Operations have a number of aircraft and ships utilized for atmospheric research, some of which includes CO$_2$ measurements. There is a plan to launch a satellite to monitor CO$_2$ (Orbiting Carbon Observatory). There are also past, present and future government funded (EPA, NASA, NOAA, DOE, etc.) field campaigns that include GHG measurements. Expanding these efforts will generate more dependable, and spatially covered observations that will build a long-term record. This would be coupled with protocols for calibration, validation, and data handling, which will increase the reliability and accessibility of the data product.

In addition to the observations, there are a number of models and emission inventories that help to better understand GHG sources. Some commonly used models include the Global Environmental Multiscale Model, Weather Research and Forecasting model coupled with chemistry (WRF-Chem), Community Multiscale Air Quality model (CMAQ), the Comprehensive Air Quality Model with Extensions (CAMx), and GEOS-Chem. The EPA has developed a Greenhouse Gas Emissions Model to estimate GHG emissions from vehicles. The Weather Research and Forecasting model (WRF) is a mesoscale weather prediction model that can be coupled with chemistry (WRF-CHEM) to simulate trace gases and aerosols (emission, transport, transformation). The EPA also develops emission inventories, which detail the emissions of a variety of sources. Tools like the Motor Vehicle Emission Simulator (MOVES)
assist in identifying some of the major pollution sources, track emissions over time, serve as model inputs to help estimate air quality, and determine the need and focus of future observations.

With all this in mind, there is interconnectivity between the observations, emission inventories, and models. The models need inputs from the observations and inventories to provide accurate estimates. The observations need models to identify areas of interest and guide future implementation. The emission inventories need observations to monitor and quantify the actual emissions from the sources. The GHGIS could manage these systems create a more efficient, cohesive research network.

The GHGIS should implement better data management strategies. This could be done by creating a GHG database that is both easily accessed and to understand, which will aid in model development and assessing the current state of GHGs (Dimotakes et al., 2011). The GHGIS should play an active role in the development of new technologies. This could be the development of new instrumentation, constructing a new model, or redefining validation/verification techniques (Dimotakes et al., 2011; Pacala et al., 2010). The GHGIS could assist in a collaborative effort or it could take on management role. In order to maintain and increase current research efforts, the GHGIS should provide support and tools training and education, thus ensuring the community has the proper knowledge and skills (Michalak et al., 2011). The GHGIS is should have the capability to identify community needs and evolve to fulfill them. This could entail directing current and future research to meet GHGIS needs or into new avenues not yet explored (Michalak et al., 2011). Along with this, the GHGIS would be able to encourage and facilitate collaborative work and generate stronger connections between research organizations, government agencies, and policy-makers (Michalak et al., 2011).
Focusing all of these efforts into one organization could make it easier to manage and simpler to fund than trying to tackle each task individually.

6.3. Critical Gaps

There are a number of gaps in knowledge concerning the carbon cycle observations. Satellites are approaching or have exceeded their intended life span and limited funding decreases the likelihood of them being replaced, emission inventories don’t cover every carbon pool, and there is an insufficient number of terrestrial and oceanic observation sites (Birdsey et al., 2009). These gaps stress the need for improvements in satellite, terrestrial, and ocean observations. Models require better process understanding and quantification, whether it is with anthropogenic, biogenic, or socioeconomic drivers (Michalak et al., 2011). With this, the development of ensemble models that incorporate multiple functions (chemical transport, atmospheric chemistry, assimilation of observations, etc.) is needed along with generation of better and transparent verification and validation tools (Dimotakes et al., 2011). Disconnects exist within the research community as well as between the research community and the needs of external organizations (agencies, policy needs, monitoring needs). As the observations, modeling, and communication improve, the translation of information to external groups (public, policy makers, agencies) will need to improve to allow these groups to make informed decisions. Brought together, these gaps pose a large barrier for scientific and economic progress.

6.3.1. Operational Gaps

As stated previously in section 6.1, the operational gaps deal with standardization (data handling, calibration, validation, verification) and implementation of new technology. Ideal observations are continuous, have wide spatial and temporal coverage, and develop a long-term record. However, when trying to quantify a global system like the processes associated with
GHGs, those three things are not quite enough. Given the variety and number of observations and models, there are many factors that can limit the efficiency and quality of the data.

Variations in calibration and validation techniques reduce the reliability of the data. Different data processing methods can introduce additional error. Greenhouse gas monitoring networks already exist for terrestrial and oceanic environments that provide a level of information, but there is still a lack of continuity, coverage, and long term records as well as a level of disconnect concerning many operational aspects (Michalak et al., 2011). The disconnect deals with the variability in instrumentation techniques used, calibration practices, and data handling. There is a need to streamline observation practices to generate better quality, easier to use, accessible data. Improvements need to be made concerning emissions inventories, terrestrial and oceanic measurements, and remote sensing.

While the current emission inventories offer valuable information, there is a need to strengthen our national GHG inventories and develop the ability to accurately estimate the GHG sources and sinks (agriculture, forestry, anthropogenic, etc.) (Pacala et al., 2010). This is especially important for CO$_2$ and CH$_4$, in which past and current variations and their uncertainties need further investigation (Michalak et al., 2011). They can be improved in a number of ways. Implementing more thorough and frequent self-reporting of inventories and utilizing the most strict Intergovernmental Panel on Climate Change (IPCC) methods for the critical GHG sources. (Pacala et al., 2010). Developing emission inventories that are more appropriatly gridded and at better resolutions. (Pacala et al., 2010). Extending the observations networks to sample over representative emitters and using this information to estimate underrepresented regions. (Pacala et al., 2010). Institutions will generate better emission inventories if the are provide with stable support (technical, financial) to sustain proper training.
and tools (Pacala et al., 2010). These improvements, among others, will help improve our ability to estimate GHG emissions and monitor trends, aiding in better decisions concerning scientific developments and policy decisions.

There are a number of observation networks that provide valuable information, but these capabilities could be improved. If all the observations are calibrated and validated differently, then there is an inherent discrepancy between them. How the data is processed and handled can have an impact on quality and ease of use. There are a multitude of factors that hinder progress in understanding GHGs and many of these factors could be eliminated or reduced by standardizing practices. The standardization of observations can lead to more reliable, easier to use datasets. The first need is to standardize the calibration and validation techniques. This applies to in situ flux measurements to remote sensing. This will create common ground between independent observations using the same techniques, increasing the reliability of all datasets. One of the biggest priorities should be set to standardize and coordinate the existing networks to act as a permanent network (Michalak et al., 2011). By bringing together flux, tower, ship, buoy, and aircraft measurements into an integrated system could generate a more cohesive network that, with stable funding, could generate a more reliable, continuous dataset (Michalak et al., 2011). The new network can institute calibration and validation methods for in situ and remote sensing observations (Dimotakes et al., 2011). Data protocols could be established across the different methods enabling better quality assurance and streamline the data handling for easier access (Dimotakes et al., 2011). This will help inform and improve models and emission inventories by providing a large, reliable, accessible GHG dataset (Dimotakes et al., 2011; Pacala et al., 2010). This system could also tackle the need for better understanding of biological processes and ocean acidification by extended observational capacity (Michalak et al.,
Existing satellite datasets of GHGs and land cover could be further utilized by coupling them observations to improve assessments of land cover, land use and change, agricultural productivity, and economic and energy activities (Dimotakes et al., 2011), which will also aid in emission inventory generation.

While models are improving, they can be limited in scope. There is a need for an ensemble model that integrates current modeling capabilities. This would include atmospheric chemical transport, biospheric models, parameterization for physical processes, variable grid resolution, comprehensive uncertainty quantification with bias detection and corrections, and atmospheric chemistry (Dimotakes et al., 2011). The model needs to be capable of handling large observation datasets and the ability to integrate future datasets (Dimotakes et al., 2011). The model needs to be capable of predicting how different climate change scenarios will affect ecosystems, biodiversity, and natural resources as well as help understand the drivers of carbon emissions (Michalak et al., 2011). Once completed, a system to test and validate these models will need to be established.

6.3.2. Scientific Knowledge Gaps

As noted in section 6.1, the scientific knowledge gaps pertain to understanding the GHG processes, developing new techniques and methodology, and issues with observations and modeling. Three overarching research questions were expressed by Michalak et al. (2011) to serve as a guide in their U.S. Carbon Cycle Science Plan:

"1) How do natural processes and human actions affect the carbon cycle on land, in the atmosphere, and in the ocean?

2) How do policy and management decisions affect the levels of the primary carbon-containing gases, carbon dioxide and methane, in the atmosphere?"
3) How are ecosystems, species, and natural resources impacted by increasing greenhouse gas concentrations, the associated changes in climate, and by carbon management decisions?”

While these questions are fairly general, they do provide a framework for directing future research. There has been extensive research over the decades devoted to these questions, but we still can’t fully answer them. This suggests that our current state of GHG research may not be sufficient enough. Answering these questions requires a more focused, coordinated effort.

Ongoing research into new methods of observations and modeling are a necessity for understanding GHG dynamics. The issue is that the development of new technologies does not always align with the scientific needs, therefore, decreasing the benefits of the new technologies. Aligning current and future developments towards GHGIS needs will increase the effectiveness of the new technology and fill knowledge gaps. This effectiveness can be further increased by providing financial and technical support, which could in turn generate more interest in development of GHG scientific efforts. This same principle can be applied to current and future projects and scientific campaigns. Aligning project goals towards GHGIS goals and providing additional support will benefit all groups involved.

While there are ongoing efforts to understand the processes controlling GHG distributions in the atmosphere, there is still much left undiscovered. Increasing efforts to understand the complicated processes dealing with oceanic, terrestrial, and anthropogenic sources and their interactions with one another is crucial for developing remediation and adaptation strategies related to climate change. This includes increasing research pertaining to land use changes (agriculture, deforestation, etc.) to ocean acidification to large scale anthropogenic emissions (power plants, cities) (Michalak et al., 2011; Pacala et al., 2010).
Increasing our monitoring capabilities will help develop our understanding of the processes and in turn, our understanding of the processes will refocus the attention towards new unexplored areas. Better understanding of emissions and sources can be achieved by extending our observation networks to underrepresented regions on a regional and global scale (Pacala et al., 2010).

6.3.3. Coordination Gaps

In section 6.1 the coordination gaps were classified as the difference disconnects that exist between groups and the issues of conveying information to external groups. The GHG issues span the world and cover many fields and therefore need an interdisciplinary strategy for understanding them. Many collaborative efforts have been made, but strengthening these connections and generating new ones will benefit the individual as well as the community. This can be accomplished through increased collaborative research. As stated earlier, there is interconnectivity between observations, emission inventories, and models. There is a positive feedback between them, so increasing our capabilities in one area helps the others become more effective. Developing the capability to accurately model and estimate GHG emissions requires the cooperation of observation research and emission inventory generation. If modelers were able to direct the observations and inventory generation to their needs it could create more accurate estimates with decreased uncertainty. Generating better emissions estimates requires the observation of key sources, which can be identified through accurate modeling. Increasing our observation capabilities and accuracy of models will lead to better emission estimates. Our understanding of GHG sources and sinks will increase with increased observations. Models and emission inventories help identify where the observations are insufficient and what the important systems to the GHG processes are. Any level of disconnect between the observations, models,
and emission inventories creates unnecessary barriers and reduces the efficiency and effectiveness of GHG research as a whole.

Even if all the gaps related to GHG science and research were closed, there is still a barrier when it comes to translation of information to external groups. In order to remediate the adverse effects of a changing climate due to GHGs, the information needs to be timely and dependable for policy-makers to make informed decisions. Just like the interconnectivity between the observations, emission inventories, and models, there is a positive feedback between research and policy. Policy makers are able to make more informed decisions if the research community addresses their needs. Likewise, the research community is able to make more scientific advancements if the policy makers provide more direction and funding. Any level of disconnect between science and policy hinders progress. Additionally, the public is disconnected from the science and policy communities. GHG issues and climate change is a global problem and the public needs to be informed in a reliable and timely manner. If properly informed, the public is able to make environmentally conscious decisions that can help in the management, adaptation, and remediation of GHG effects and climate change. In turn, a well informed public will push policy makers for more GHG research, which in turn directs policy makers to important issues, which in turn provides funding and direction for the science community. Everything is so interconnected that any level of disconnect hinder progress, so bringing it all together becomes imperative to building an efficient and effective GHGIS.

6.4. Proposed Initial Steps

A collaborative effort is needed to bring the appropriate organizations together and close the gaps associated with greenhouse gases. While the GHGIS would entail many organizations, it would be beneficial to have a management structure to organize the collaborative efforts and
facilitate integration and coordination between capabilities and participants. Ideally, the management could be housed within an existing organization that already has the important collaborative connections. One potential candidate is the United States Global Change Research Program (USGCRP). USGCRP already has a significant capacity for fostering interagency collaboration, and its new decadal strategic plan (“A National Global Change Research Plan: 2012-2021”) gives prominent place to the need for a robust research program to support decision-making about greenhouse gases mitigation. Different elements within the USGCRP could occupy particular roles to collectively tackle the various gaps.

The USGCRP consists of multiple subgroups with the capability to function independently while still maintaining collaboration with the other groups. These groups include the National Climate Assessment (NCA), Carbon Cycle Interagency Working Group (CCIWG), the Global Change Information System (GCIS), Interagency Observations Working Group (IOWG), Interagency Group on Integrative Modeling (IGIM), and the Process Research Coordinating Committee. In addition, however, USGCRP would need to build enhanced connectivity with other elements of the federal government that are not part of the core of USGCRP, including EPA’s Office of Air and Radiation, the energy and technology programs with the Department of Energy, and the State Department, to ensure alignment with climate and energy policy goals.

The operation gaps can be handled by the CCIWG, GCIS, and NCA. The CCIWG is capable of handling or playing a part in closing all of the operation gaps. They can help implement standardization of methods, calibrations, verifications, validations, and other aspects into GHGIS monitoring efforts. The GCIS can assist the CCIWG with standardization and help streamline the data assimilation. The scientific knowledge gaps are a bit broader in scope, but
the capability to handle them still lies within USGCRP. The observation knowledge gaps can be handled through the combined effort of the CCIWG and IOWG. Both of these groups play a role in observations and can help direct the current and future research to increase GHG knowledge. The knowledge gaps concerning modeling would lie under the capabilities of the GCIS and IGIM. The ability to increase model skill and guide the development of new techniques and verification methods lies within these groups. To close the knowledge gaps concerning process understanding can be handled by the CCIWG. The group already deals with the observation networks and data, which enables the guidance of information to generate a better understanding of GHG processes.

The USGCRP already engages in interagency collaborations, however, as mentioned before there is a need for a federal effort to create links to mitigation and act as an administrative and policy driver for the GHGIS. This overarching federal effort combined with the strong interagency ties of USGCRP will close the communication gaps. In combination with the NCA’s report on the state of the climate, this organization will have multiple venues in which to translate the information to the public, scientists, agencies, and policy makers.

The first step towards building a GHGIS would be to create an exploratory committee. This committee can begin with only a few people and the purpose would be to generate interest from important groups and agencies. This initial effort easily fits within the usual operations of the USGCRP, in which they are in constant contact (meetings, email, phone calls) with a number of people and agencies. Once the exploratory committee is formed, they would be tasked with an initial review of GHGIS capabilities. This would include the assessing the need, structure, and feasibility of constructing the organization, which could be accomplished through meetings or conference calls.
With the initial assessment of GHGIS capabilities complete, this information can then be used to recruit any interested parties. The objective would be to hold a larger scale, collaborative workshop pertaining to what the exploratory committee has proposed for a GHGIS and any inherent issue that may have developed. This workshop would further assess the GHGIS need, structure, and feasibility. Additionally, this forum would suit well for identifying any additional key gaps in current GHG research that the GHGIS could solve. With the preliminary GHGIS issues discussed, the workshop could serve as a perfect forum to establish a timeline for generation of the GHGIS. This would entail assessing the level of funding needed, identifying the goals and estimate how long it will take to reach an achievable level of success, and discuss how to direct current and planned research activities to align with GHGIS needs. Due to the large amount of required tasks, this could be broken down into multiple workshops, which would enable increased participation due to additional availability.

A logical step would be to include a level of GHGIS assessment in the 2017 National Climate Assessment. The quad-annual report already brings together a large number of groups, organizations, and agencies and is the perfect forum for assessing the GHGIS capabilities and progress. The 2017 NCA could focus on prioritizing key knowledge gaps to tackle, develop long-term goals, establish a means for assessing the progress towards achieving said goals, and layout a timeline for implementation of GHGIS strategies.
6.5. References


CHAPTER 7: SUMMARY AND CONCLUSIONS

7.1. Summary

Chapter 1 gave an overview of the motivation for the development of the IVOC sampler. Chapter 2 was presented the experimental methods and techniques. It gave an overview of the theory of operation of the proton transfer reaction mass spectrometer to illustrate how its operation was modified in this research to allow for measurement of IVOC compounds by thermal desorption. The governing reactions and physics of the PTR-MS principle of measurement were described and how they affect the interpretation of data. The chapter also described the development and operation of the IVOC Sampler, including the construction and automation of the sampler and performance characterization including tests done in the lab and in the field. The chapter covered interpretation and processing of the data, how the system was calibrated, and method detection limits. It demonstrates the capability of the IVOC sampler to discriminate against VOC species that interfere with IVOC responses.

Chapter 3 was an experimental methods manuscript submitted in June 2013 to the journal Atmospheric Measurement and Techniques. Laboratory experiments showed the sensitivity of the PTR-MS to n-alkanes and sampling of vehicle fuels helped identify species that could be important in vehicle exhaust. It detailed the operation and fidelity of the thermal desorption PTR-MS technique for measuring IVOC compounds. The IVOC sampler was able to discriminate against gasoline exhaust, thus removing any VOC interferences. The IVOC sampler was capable of measuring C_{12} – C_{18} alkanes and their abundance within diesel exhaust was 76% of the abundance of alkylbenzenes. Thermal desorption sampling and low Townsend number PTR-MS analysis is a viable approach for providing quantitative information on the total abundance of IVOC species in diesel exhaust.
Chapter 4 presented a manuscript that detailed the deployment of the PTR-MS and IVOC sampler during the CARES field experiment. The PTR-MS observed both anthropogenic and biogenic sources influencing the site evidenced in up to 3 ppbv of toluene during large vehicle pollution events and the diel patterns in isoprene. Significant photochemistry was also observed with diel patterns in formaldehyde, acetaldehyde, and other photoproducts. The IVOC sampler was also able to quantify the abundance of IVOC alkanes, which reached nearly 3 ppbv during the large pollution events. Their abundance was found to be approximately 40% lower than the abundance of alkylbenzenes. Investigation of the pollution events showed that the IVOC alkanes were 30 to 40 times higher than the concentration of soot, a common diesel exhaust tracer. The measured IVOC alkane abundance implied a significant pool of reactive compounds, comparable to the abundance alkylbenzenes, and should be considered in SOA formation in urban air quality.

Chapter 5 presents a manuscript detailing the deployment of the PTR-MS and IVOC sampler during engine exhaust chamber monitoring at LRRI. It briefly detailed the laboratory setup and instrumentation, along with details about the IVOC sampler method. It reported the relative abundances of IVOC species within gasoline and diesel exhaust. Discussion of the relative abundance to CO$_2$ estimated the potential emission rates of IVOC species. Looking at the role of engine load, it was noted that IVOC emissions are lowest under a high load, highest under typical loads, and the low engine load emissions are a bit lower than the typical load. It presented a metric for quantifying the relative contribution of gasoline and diesel exhaust to a mixture and showed that the predicted exhaust signature reflected the observed one. It also discussed the SOA formation potential of IVOC species within diesel exhaust and noted that our results supported the hypothesis of Robinson et al. (2007) that suggests more than 85% of diesel exhaust SOA formation is from IVOC species.
Chapter 6 presented a policy paper resulting from the APT internship experience. The chapter described the need and process for establishing a greenhouse gas information system (GHGIS) for the United States. It summarized some of our current GHG monitoring capabilities that could benefit from integrating into a GHGIS. The need for integration was demonstrated through the critical gaps concerned with scientific knowledge, monitoring operations, and communication. Initial steps for creating a GHGIS were proposed by utilizing USGCRP capabilities. USGCRP already has the important connections within the GHG research community and is a potential agency capable of handling GHGIS integration and management.

7.2. Conclusions

The IVOC sampler has potential to provide a benefit to atmospheric research, especially concerning urban air quality. It is a viable method for measuring IVOC compounds, which are fairly uncharacterized. Our estimation of diesel exhaust SOA formation supported the hypothesis of Robinson et al. (2007), suggesting that IVOCs produce at least a factor of 5.7 more SOA than traditional SOA precursors. This stresses the need for a better understanding of their urban abundance. With the complexity of diesel exhaust making it difficult to measure, there were some other key groups that were identified that could play as critical a role as the IVOC alkanes. The naphthenic monoaromatics were fairly abundant within both exhausts, typically the 4th most abundant group after the alkenes and alkanes, alkylbenzenes, and oxygenated compounds. This suggests they can also play a critical role in SOA formation and additional research should be focused on understanding their abundance.

There was also a surprising similarity between the gasoline and diesel exhausts observed by the PTR-MS. The combustion of either fuel seems to lead to the same constituents at similar relative abundances. The diesel exhaust did have a higher abundance of IVOC species, but the
gasoline exhaust contained more than expected. These IVOC species are likely the result of lubricant oils in the exhaust, but a source of IVOC species nonetheless. This leads to the notion that gasoline exhaust could contribute a fairly significant pool of SOA precursors in addition to the more traditional alkylbenzenes. The proposed metric of using the ratio of relative abundance to \textit{m/z} 135 could prove very useful. These abundance ratios could help tell the difference between vehicle exhaust plumes and other sources and has potential to assess the relative contribution of gasoline and diesel vehicles in a complex mixture. This would provide a valuable source assessment to ambient observations and could be integral in understanding vehicle related pollution issues and SOA formation.
APPENDIX A: DAQFACTORY AUTOMATION SEQUENCES

//IVOC OPERATION


// Sample Mode  ( 5 seconds + Time_Sample) - Time_Sample =

Valve_BF = 5 // (5 == OFF), 0==ON
Valve_Carrier = 5 // (5 == OFF), 0==ON
Valve_Sample = 5 // (5 == OFF), 0==ON
Valve_Inlet = 0 // (5 == OFF), 0==ON

Heat_Enable = 0 // (5 == ON), 0==OFF
Tube_Temp_Set = 10

Mode_State = 3
Valve_TW_Pos_B() // VOC Sample mode (old mode)
Delay(1)

Valve_CZ_Home() // CZ Valve is on Sample Port (# 1)
Delay(4)

If(Zero_Trigger == 1)
    Valve_CZ_Step() // CZ Valve is on Dry Nitrogen Port (# 2)
    Delay(4)
EndIf

Tube_Temp_Set = Temp_Sample
If(Temp_Sample > 50)
    Heat_Enable = 5
EndIf
Valve_Sample = 0 // Begin Sample
Start_Time_Sample = SysTime()%3600/60

Delay(Time_Sample) // Sample Time


// Purge Mode - Dry N2 at high temp (128 seconds + Time_Purge) - Time_Purge=120 -> 248 = 4:08


Mode_State = 7
Valve_CZ_Home() // CZ Valve is on Sample Port (# 1)
Delay(4)
Valve_CZ_Step() // CZ Valve is on Dry Nitrogen Port (# 2)
Delay(4)

//Begin Purge

Start_Time_Purge = SysTime()%3600/60
Heat_Enable = 5
If(Temp_Purge < 50)
    Heat_Enable = 0
EndIf
Tube_Temp_Set = Temp_Purge
Delay(Time_Purge)
    //Purge Cooldown
    Heat_Enable = 0
    Tube_Temp_Set = 10
Delay(120)

///////////
// Measure Mode ( 111 seconds + Time_Measure + MID delay time ) - Time_Meas=300, MID
delay = 60 -> 471 = 7:51
///////////

Mode_State = 1

Valve_CZ_Step() // CZ Valve is on Capped Port (# 3)
Delay(4)

Delay(30) // Pump Down Time

Valve_Sample = 5
Delay(2)

While(IVOC_Mode<2)
Delay(1)  // Delay until MID file has switched
EndWhile

Start_Time_Measure = SysTime()%3600/60
Valve_Inlet = 5
Delay(5)

Valve_TW_Pos_A()  // IVOC Sample mode (new mode)
Delay(30)  // Additional Pump Down

Valve_Carrier = 0  // Begin Measure
Delay(30)
Heat_Enable = 5
Tube_Temp_Set = Temp_Measure
Delay(Time_Measure)  // Measure Time

//Implementing Ramping Temp
//Tube_Temp_Set = 120
//Delay(60)
//Tube_Temp_Set = 150
//Delay(90)
//Tube_Temp_Set = 165
//Delay(150)
//Tube_Temp_Set = 165
//Delay(150)

Valve_Carrier = 5  // Stop Measure
Delay(10)

//VOC MODE

///////////
// Mode_Backflush (210 seconds + Time_Backflush) - Time_BF = 180 -> Total Time = 390 -> 6:30
///////////

Mode_State = 2
Valve_TW_Pos_B()  // VOC Sample mode (old mode)
Delay(10)

Valve_Inlet = 0 // Measure from normal inlet
Delay(2)

Valve_CZ_Step() // CZ Valve is on Backflush Port (# 4)
Delay(4)

Valve_BF = 0 // Begin Backflush
Start_Time_Backflush = SysTime()%3600/60
Tube_Temp_Set = Temp_Backflush
Delay(Time_Backflush) // Backflush time

Heat_Enable = 0
Tube_Temp_Set = 10

Delay(180) // Backflush cooldown

Valve_BF = 5 // Stop Backflush
Delay(2)

Valve_CZ_Home() // CZ Valve is on Sample Port (# 1)
Delay(4)

Valve_CZ_Step() // CZ Valve is on Dry Nitrogen Port (# 2)
Delay(4)

Valve_CZ_Step() // CZ Valve is on Capped Port (# 3)
Delay(4)

APPENDIX B: ADDITIONAL SETUP AND COMMUNICATION

A. Flow Setup

The setup of the plumbing system is relatively straight forward. Most of the parts are already configured within the IVOC system box and merely require connections to the bulkheads outside of the box. There are 5 bulkheads in total that need to be connected; 3 in the back and 2 in the front. The three in the back are for the desorb, backflush, and sample flows.
**Desorb and Backflush Connections**

The desorb and backflush both require dry N2 and can come from the same source, but it is crucial to at least have the desorb N2 run through a hydrocarbon trap to reduce any contaminants and from a well pressure regulated source. When connected to a liquid N2 dewer, fluctuations in the desorb flow have been observed on the order of 10% of the flow due to fluctuations in regulated pressure. It is often best practice to use a compressed gas standard N2 source for the desorb to avoid such fluctuations. The desorb flow was typically 25 sccm and the backflush flow is typically ~100 sccm. There are also two bulkheads at the front of the IVOC system box that connect to the 2-position actuator. The desorb flow is connected to port 1 and the backflush is connected to port 5. Note that the backflush and sample flows are connected to the same bulkhead and are connected to the 2-position actuator port.

**Sample Flow Connections**

The sample flow is managed through the use of a diaphragm pump (Gast) and is hooked up in two locations. The first is to connect the pump to the bulkhead at the back of the IVOC system box. The bulkhead is connected to the MFC that controls the sample flow which is typically set to 40 sccm. In addition, the pump is also connected to the sample line to supplement this 40 sccm sample flow to make sure there is sufficient flow and allow for efficient sampling. This flow can be regulated by a rotometer or needle valve and is typically set around 1 slpm. The sample line is connected to port 1 of the 4-port multi-position valve. The sample flow is also connected to the 2-position actuator port 5 from a bulkhead located at the front of the IVOC system box. Note that the backflush and sample flows are connected to the same bulkhead and are connected to the 2-position actuator port.

**Multi-position Electric Actuator**
This valve has 5 port connections and allows for the selection between four different flow paths. The common port of this valve is connected to port 4 of the 2-position actuator. The setup of the multi-position electric actuator (CZ valve) coincides with the IVOC system mode. The first step is sampling mode and port 1 of the CZ valve is selected. This port connects the sample line to the 2-position actuator and allows for sampling onto the Tenax.

Once sampling is complete, the IVOC system switches into purge mode in which the CZ valve changes to port 2. This port is connected to a constant flow of dry N\textsubscript{2} that is regulated to a flow $\geq 100$ sccm by a needle valve. The N\textsubscript{2} source can be the same as provided for the backflush flow.

Once purge is complete, the IVOC system switches into measure/desorb mode in which the CZ valve changes to port 3. This port is capped off to allow the IVOC system to pump down and reduce any pressure spikes. When the 2-position actuator switches into measure position (position B) there is a pressure spike caused by the higher pressure in the IVOC system lines compared to the drift tube. If this pressure spike is too large it can result in the drift pressure being too high (\textasciitilde 3 mbar) and triggering a safety protocol which turns off power to the drift chamber. The reason for this safety measure is to prevent any electrical arching that can occur in the drift tube if the pressure is too high. To prevent this from happening, the IVOC system lines are pumped down by switching the CZ valve to the capped port 3 and keeping the sample valve open to allow the diaphragm pump to pump down the lines. Typically, 30 seconds has been found to be sufficient to reduce the pressure spike to a reasonable level, but additional time can be added if needed.

Once measure/desorb is complete, the IVOC system switches into backflush mode in which the CZ valve changes to port 4. This port is simply connected to a tube and merely acts as
a vent for the backflush flow. This tube can be connected to an exhaust line to prevent any contamination to the room, especially if the sampling includes hazardous species.

Two Position Microelectric Valve Actuator and Tenax trap

This valve has 6 ports, which are connected differently depending on what position the valve is in. In position, A the port connections are 1 to 6, 2 to 3, and 4 to 5. In position B the port connections are 1 to 2, 3 to 4, and 5 to 6. The system is in position B during sample, purge, and backflush modes and in position A during the measure mode. Port 2 of the 2-position actuator is connected to the PTR-MS custom sample ring by a ~17” long 0.01” ID tube that is electrically isolated. The reason for the small ID and the added length is to reduce the pressure spikes that occur when switching to measure mode. The desorb N2 for is connected to port 1, the CZ valve is connected to port 4, and the sample/purge/backflush flows are connected to port 5. The Tenax trap is connected to ports 3 and 6 and is mounted to the IVOC box by the M4 rods.

B. DaqFactory Setup

Solenoid Valve Control

The switching of the sample, measure, backflush, and PTR-MS inlet solenoid valves are controlled by 4 solid state relays (SSRs). Channels 7 to 10 in DaqFactory are configured to output either 0 or 5 V to the corresponding SSR. When the channel outputs 0 V, the SSR disconnects the power to the solenoid valve, setting the valve in its normal state. The normal state for the two-way solenoid valves (sample, backflush, PTR-MS inlet) is closed and for the three-way valve (measure) connects the common port to the port perpendicular to the common (top port). When the channel outputs 5 V the SSR connects the power, which switches the valve
into the energized state. The energized state for the two-way solenoid valves is open and for the three-way valve connects the common port to the parallel port.

Two Position Microelectric Valve Actuator

The communication to the 2-position actuator is through a manual controller cable connection that consisted of 10 wires. The wires are identified as 1 to 10 starting with the red wire. Two were used to switch the valve state (5 and 6) and two were used to monitor the valve state (1, 3 and 4). The 2-position actuator position is switched when an input is subjected 0.3 s 5 V pulse. Switching to states A and B were controlled through wires 5 and 6 respectively. Dig Out channels 12 and 13 were connected to wires 5 and 6 respectively and configured to toggle between 0 and 5 V. Custom DaqFactory sequences were written to toggle the channel to 5 V for 0.3 s. In order to record which state the actuator is in, A to D channels 2 and 3 were configured to monitor the actuator outputs from wires 4 and 3 respectively, which output 0 V to signify the actuator is in that state (asserted) and 5 V when the valve is in the other state (deasserted).

Multi-position Electric Actuator

The multi-position electric actuator (CZ Valve) contains 5 ports and communication is through an interface cable connection that consists of 20 colored wires. The wires are identified by color with each color repeating twice. Three wires were used to switch the 4-port valve. Starting at the brown end, the first purple, gray, and white wires were used. The purple wire enables switching to the home position (port 1) and is controlled with channel 15, the gray wire enable switching to the next port and is controlled with channel 14, and the white wire is connected to the ground. The valve was switched by a 0.3 s 5 V pulse to the desired wire.

Tenax Heating and PID
The heating system uses the LabJack analog output (DAC0) and a PID algorithm to provide a variable voltage input into the solid state relay control module. The SSR control module regulates an SSR connected to the Hammond power transformer and the input signal to the SSR control module has a linear relationship to the current output from the power transformer. The SSR control module input signal is controlled by a PID algorithm that keeps the temperature constant once the desired temperature is reached.

*MID Switching*

The MID switching was accomplished through communication with the PTR-MS Measure software. The PTR-MS is outfitted with 5 switch connections that enable the toggling of external valves. A custom pinned connector was connected to switch 1 and used to create a connection between a 5 V terminal connection to DaqFactory terminal FIO4. DaqFactory channel 4 is set to monitor the voltage. When the PTR-MS software had the connection toggled on, the circuit was connected and the 5 V from the LabJack was measured with channel 4. When the PTR-MS software had the connection toggled off, the circuit is disconnect and DaqFactory channel 4 measures 0 V. The MID switching is controlled by the PTR-MS software, but the IVOC system is controlled with DaqFactory, so there was a need to have the PTR-MS software signal DaqFactory when the switching has occurred.

*Mass Flow Controllers*

While the flows are controlled through a POT located on the boards themselves, the LabJack is setup to monitor the flows of each MFC. The A to D channels 5 (FIO5), 6 (FIO6), and 7 (FIO7) were setup to measure the sample, backflush, and desorption flows respectively. The MFCs output a 0-5V signal, which corresponds to a particular flow depending on the MFC.
A 5 V signal corresponds to 1000, 500, and 50 sccm for the sample, backflush, and desorption flows respectively.
APPENDIX C: DATA PROCESSING

////////////////////////////////////////////////////////////////////////////////////////////////////////////////
// 1) Load PTR-MS IVOC Data
// 2) Load DaqFactory IVOC Data
// 3) Paste in MassNumber Wave
// 4) Rename PTR-MS time wave 'Date_Time_IVOC'

Macro Prep_Waves_Lab()  //Check the data in excel to make sure everything here applies
Date_Time_IVOC -=8*60*60 // This corrects the data from UTC to PDT. This will change. Pay
attention to timezone
m21 *=490  //Correct the data to MHz. This is commented out because it is accounted for in the
Norm_mXX_lab() function
//TheTime += date2secs(1970,1,1) //DaqFactory time is seconds since 1970, Igor is seconds
since 1904, so adding the extra time to DF
SetScale d 0,0,"dat", Date_Time_IVOC
//SetScale d 0,0,"dat", TheTime
End Macro

Macro Norm_mXX_lab()
silent(1)
variable b
string num, Name, Name2
b=1
Do
Name = MassNumber[b]  //Creates a reference to mXX at row b
Name2 = MassNumber[b]+"_norm"  // Creates a reference to mXX_norm at row b
Make/O/D/N=(numpnts(m21)) $Name2  //Makes the mXX_norm wave
$Name2 = $Name / m21 * 10^6  //Normalizes mXX_norm to m21
b+=1  //Repeat the same thing for the next mXX
While(b<=numpnts(MassNumber))
Make/O/D/N=(numpnts(MassNumber)) Area_Start  //Stores where the desorption area
integration will begin
Make/O/D/N=(numpnts(MassNumber)) Area_Stop  //Stores where the desorption area
integration will end
Make/O/D/N=(numpnts(MassNumber)) Avg_Zero_Flag  //Stores a flag for the zeros. The flag
refers to user judgement of the zero. See below for flag variables
Make/O/D/N=(numpnts(MassNumber)) Data_Flag  //Stores a flag for the data. The flag refers to
user judgement of the zero. See below for flag variables

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Area_Start = 0  //Set to zero by default
Area_Stop = 120 // Area calc is for entire peak. Set to 120 by default
Avg_Zero_Flag = 1 //Flag all zeros as good by default
Data_Flag = 1  //Flag all data as good by default

//Flag variables
// 0 = bad/omit data
// 1 = good data
// 2 = low signal. The signal at this mXX is low and may not be significantly different from zero
// 3 = no signal. There is no data at this particular mXX
// 4 = avg zero may not work for mXX. The zeros are very variable or the conditions have changed that bring the zero to question.
// 5 = Peak doesn't go down to zero. The desorption peak is exceptionally large and does not reach zero by the end of desorption mode

Area_Base_Width()  //Runs the Area_Base_Width function

End Macro

Macro Number_Peaks_Lab()
Make/O/D/N=(numpnts(Date_Time_IVOC)) Number_Wave
Number_Wave = 0
NP_Lab_alt(0, 0, m21_trip*10^6, 0, Date_Time_IVOC, m21, Number_Wave)
//NP_Lab(0, 0, m21_trip*10^6, 0, Date_Time_IVOC, m21, Number_Wave)
// Have to change num2 around to capture peaks correctly
Check_Peak_Numbers()
End Macro

Function NP_Lab(i, num1, num2, num3, W1, W2, W3)
// NP(0, 0, 10^6, 0, Date_Time_IVOC, m21, Number_Wave)
// i = counter variable
// num1 = counter stop
// num2 = differing condition
// num3 = peak number
// W1 = Date_Time_IVOC
// W2 = m21
// W3 = Number_Wave
variable i, num1, num2, num3
Wave W1, W2, W3
num1 = numpnts(W1) //num1 is the number of points in Date_Time_IVOC wave
num3 = 1  // counter
For(i=0; i<=num1; i+=1)
    If(W2[i] >= num2)
        W3[i,i+120] = num3
        num3+=1
        i+=120
        //num2+=0.25 *10^6
        //If(num2>4.75*10^6)
        //    num2 = 4.8*10^6
        //EndIf
    EndIf
EndFor
End Function

/////////////////////////////////////////
/////////////////////////////////////////
Macro Identify_Peaks_Lab()
// Have to populate waves manually
silent(1)
variable i, k
string Name
i=0
WaveStats Number_Wave
k = V_Max + 1
Name = "Peaks_Zero"
If(exists(Name) == 0)
    Make/O/D/N=(k) Peaks_Zero  // 1 = Amb, 2 = 100C
    Peaks_Zero =  0
EndIf
Name = "Peak_Numbers"
If(exists(Name) == 0)
    Make/O/D/N=(k) Peak_Numbers
EndIf
Do
    Peak_Numbers[i] = i
    i+=1
While(i<k)
Name = "Peaks_Cals"
If(exists(Name) == 0)
Duplicate/O Peaks_Zero Peaks_Cals // Number the different Cals starting with 1
Peaks_Cals = 0
EndIf

Name = "Peaks_Temps"
If(exists(Name) == 0)
Duplicate/O Peaks_Zero Peaks_Temps // Outside Purge Temperature
Peaks_Temps = 0
EndIf

Peak_Num_Table_Lab()
End Macro

Macro Build_Peaks_Lab()
silent(1)
variable i, n, b
string num, Name, Name2, Name3
wavestats/Q Number_Wave
n=V_Max
b=2
i=1
Do
   Do
      num = num2str(i)
      Name = "Data_"+MassNumber[b]+"_"+num
      Name2 = "Data_"+num+"_Time"
      Name3 = MassNumber[b]+"_norm"
      Make/O/D/N=(numpnts(Date_Time_IVOC)) $Name
      $Name = nan
      Make/O/D/N=(numpnts(Date_Time_IVOC)) $Name2
      $Name2 = nan
      BP_Lab(0,0,i,0,date_time_ivoc,Number_Wave,$Name,$Name2,$Name3)
      Redimension/N=(150) $name
      Redimension/N=(150) $name2
      i+=1
   While(i<=n)
i=1
b+=1
While(b<=numpnts(MassNumber))
End Macro
/////////////////////////////////////////
Function BP_Lab(i, num1, num2, num3, W1, W2, W3, W4, W5)
// IP(0,0,0,0,date_time_ivoc,Number_Wave,$Name,$Name2,$Name3)
// W1 = date_time_ivoc
// W2 = Number_Wave
// W3 = $Name or Data_mXX_num
// W4 = $Name2 or Data_num_Time
// W5 = $Name3 or mXX_norm
variable i, num1, num2, num3
wave W1, W2, W3, W4, W5
num1 = numpnts(W1)
For(i=0;i<=num1;i+=1)
    If(W2[i]==num2)
        W3[num3] = W5[i]
        W4[num3] = W1[i]
        num3+=1
    EndIf
EndFor
End Function
////////////////////////////////////////////////
////////////////////////////////////////////////
Macro Zeros_Average_Lab()
silent(1)
variable b, i, s, k, r, n, m
string num, Name, Name2, str1, str2, Name3, Name4, Name5
b=2
i=1
k=0
r = 0
n = 1
wavestats Peaks_Zero
m = V_max
Do
Do
    num = num2str(Peak_Numbers[i])
EndDo
EndDo

Name = "Data_"+MassNumber[b]+"_"+num
Make/O/D/N=(numpnts($Name)) TempWave1
TempWave1 = 0
Do
  If(Peaks_Zero[i] == n)
    num = num2str(Peak_Numbers[i])
    Name = "Data_"+MassNumber[b]+"_"+num
    TempWave1 += $Name
    k+=1
  EndIf
  i+=1
EndDo
While(i<=numpnts(Peak_Numbers))
Name3 = "Avg_Zero_"+MassNumber[b]+"_"+num2str(n)
TempWave1 /= k
str1 = "Avg_Zero_"+MassNumber[b]+"_"+num2str(n)
If(exists(str1) == 1)
  KillWaves $Name3
EndIf
Rename TempWave1, $Name3

k=0
r=0
i=1
n+=1
While(n<=m)
  n=1
  b+=1
  While(b<=numpnts(MassNumber))
EndWhile
EndWhile
End Macro

////////////////////////////////////////////////////////////////////////////////
/////////////////////////////////////////////////// //////////////////////////////
Macro Find_Base_Width()
silent(1)
variable i,q,b,x,m
string num, num2
string N_Data, N_1SD_Zero, mXX
i=0
b=0 //MassNumber Counter for beginning
x=1 // Peak number
q=0
wavestats/Q Peaks_Cals
m = V_max // Highest peak number

mXX = "m"+num2str(Graph_mXX)

Do
b+=1
While(stringmatch(MassNumber[b], mXX)==0)

Make/O/N=(m+1) TempStart
TempStart = nan
Make/O/N=(m+1) TempStop
TempStop = nan

    Do
        num = num2str(x)
        N_Data = "Data_"+mXX+"_"+num
        N_1SD_Zero = "Avg_Zero_"+mXX+"_1SD"

        // Find Base Width for mXX with good avg zeros
        If(Peaks_Zero[x] == 0)
            If(Avg_Zero_Flag[b]==1 || Avg_Zero_Flag[b]==2 || Avg_Zero_Flag[b]==3)
                Do
                    WaveStats/Q/R=(i-1,i+1) $N_Data
                    If(V_Avg > $N_1SD_Zero[i] || i==20)
                        TempStart[x] = i
                        q=1
                    EndIf
                    i+=1
                While(q==0)
                q=0
                WaveStats/Q TempStart
                Area_Start[b] = round(V_Avg)
                i+=10

                Do
                    WaveStats/Q/R=(i-1,i+1) $N_Data
If(V_Avg <$N_1SD_Zero[i] || i==50)
    TempStop[x] = i
    q=1
EndIf
i+=1
While(q==0)
    q=0
    WaveStats/Q TempStop
    Area_Stop[b] = round(V_Avg)
EndIf
EndIf
i=0
q=0
x+=1
While(x<=m)

End Macro

Macro Calc_Areas_Field()

variable i,k, n, q,b,r, diff, p, z, e, m
string num
string N_Data //Name of Data Wave "Name"
string N_Resp //Name of response wave (Data - Zero) "Name2"
string N_Area //Area Wave "Name3"
string N_Area_1SD // Area under avg zero + 1SD
string N_Area_Zero //Area under avg zero
string N_Peak_Error //Error of the data wave
string N_Avg_Zero //Zero wave "Name4"
string N_1SD_Zero //Zero + 1SD
string N_Start //Temp Wave for start points
string N_Stop //Temp Wave for stop points
string N_BW_Flag //Flag the value if base width is bad (means there is not much of a peak)
                       // 0 = no peak, 1 = good BW, 2 = High Stop Point, 3 = High Start
Point, 4 = High start/stop point

i=1
//b=2
//b=4
b=29
k=1
wavestats Number_Wave
r=V_Max
print r
Do
    N_Area = "Area_"+MassNumber[b]
    Make/O/N=(r+1) $N_Area
    $N_Area = 0

    N_Area_1SD = "Area_Zero_"+MassNumber[b]+"_1SD"
    Make/O/N=(r+1) $N_Area_1SD
    $N_Area_1SD = nan

    N_Area_Zero = "Area_Zero_"+MassNumber[b]
    Make/O/N=(r+1) $N_Area_Zero
    $N_Area_Zero = nan

    N_Peak_Error = "Peak_Error_"+MassNumber[b]
    Make/O/N=(r+1) $N_Peak_Error
    $N_Peak_Error = nan

    N_BW_Flag = "Flag_BW_"+MassNumber[b]
    Make/O/N=(r+1) $N_BW_Flag
    $N_BW_Flag = 0
    $N_BW_Flag[0] = nan

    N_Start = "Start_Point"
    Make/O/N=(r+1) $N_Start
    $N_Start = nan

    N_Stop = "Stop_Point"
    Make/O/N=(r+1) $N_Stop
    $N_Stop = nan

Do
If(Peaks_Zero[i] == 0)
    num = num2str(Peak_Numbers[i])
    N_Data = "Data_"+MassNumber[b]+"_"+num
    N_Avg_Zero = "Avg_Zero_"+MassNumber[b]
    N_1SD_Zero = "Avg_Zero_"+MassNumber[b]+"_1SD"

// Find the beginning of the peak
    Do
        n+=1
        While($N_Data[n] < $N_1SD_Zero[n] && n<11)
            $N_Start[i] = n
    EndIf

// If falsely detected beginning
    Do
        If($N_Data[n] < $N_1SD_Zero[n])
            // print "Need New Start"
            Do
                n+=1
                While($N_Data[n] < $N_1SD_Zero[n] && n<11)
                    $N_Start[i] = n
            EndIf
        EndIf
    EndIf

// Find end of peak
    n = $N_Start[i]
    Do
        n+=1
        While($N_Data[n] > $N_1SD_Zero[n] && n <75))
            $N_Stop[i] = n
    EndIf

$N_BW_Flag[i] = 1

If($N_Start[i] > 10)
    $N_BW_Flag[i] = 3
EndIf
If($N_Stop[i] > 50)
    $N_BW_Flag[i] = 2
EndIf
If($N_{Start}[i] > 10 \&\& N\_Stop[i] > 50) $N\_BW\_Flag[i] = 4
EndIf

n = $N\_Start[i]
Do
//q += ($N\_Data[n] + $N\_Data[n+1]) / 2 * 4.04 // Midpoint between the points multiplied by the time between them
//p += ($N\_1SD\_Zero[n] + $N\_1SD\_Zero[n+1]) / 2 * Cycle\_Time
// Midpoint between the points multiplied by the time between them
//z += ($N\_Avg\_Zero[n] + $N\_Avg\_Zero[n+1]) / 2 * Cycle\_Time
//e += sqrt((N\_Data[n] + $N\_Data[n+1]) / 2)
q += $N\_Data[n]
p += $N\_1SD\_Zero[n]
z += $N\_Avg\_Zero[n]
e += sqrt($N\_Data[n])
n+=1
While(n < $N\_Stop[i])
$N\_Area[i] = q * Cycle\_Time
$N\_Area\_1SD[i] = p * Cycle\_Time
$N\_Area\_Zero[i] = z * Cycle\_Time
$N\_Peak\_Error[i] = e * Cycle\_Time
n=0
q=0
p=0
z=0
e=0
EndIf
i+=1
While(i<=numpnts(Peak\_Numbers))
i=0
b+=1
While(b<=4)
//While(b<=6)
//While(b<=numpnts(MassNumber))

End Macro

                    

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Macro Calc_Resp_Field()

variable b, r

string N_Resp //Name of response wave (Data - Zero)
string N_Resp_1SD //Name of response wave (Data - Zero - sigma)
string N_Area //Area Wave "Name3"
string N_Area_1SD //Area under avg zero + 1SD
string N_Area_Zero //Area under avg zero
string N_Peak_Error //Error of the data wave

b=2
wavestats Number_Wave
r=V_Max
print r

Do

    N_Area = "Area_"+MassNumber[b]
    N_Area_1SD = "Area_Zero_"+MassNumber[b]+"_1SD"
    N_Area_Zero = "Area_Zero_"+MassNumber[b]
    N_Peak_Error = "Peak_Error_"+MassNumber[b]

    N_Resp = "Area_Resp_"+MassNumber[b]
    Make/O/N=(r+1) $N_Resp
    $N_Resp = nan

    N_Resp_1SD = "Area_Resp_"+MassNumber[b]+"_1SD"
    Make/O/N=(r+1) $N_Resp_1SD
    $N_Resp_1SD = nan

    $N_Resp = $N_Area - $N_Area_Zero
    $N_Resp_1SD = $N_Area - $N_Area_1SD

    b+=1
While(b<=numpnts(MassNumber))

End Macro

////////////////////////////////////////////////////////////////////////////////////////////////////////////////////////////


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