DEVELOPMENT AND APPLICATION OF THERMAL/OPTICAL-QUADRUPOLE MASS SPECTROMETRY FOR QUANTITATIVE ANALYSIS OF MAJOR PARTICULATE MATTER CONSTITUENTS

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Abstract

A new technique that couples a Desert Research Institute (DRI) Model 2001 Thermal Optical Carbon Analyzer (TOA) to an electron impaction ionization-quadrupole mass spectrometer (EI-QMS) is developed to analyze major chemical constituents of particulate matter (PM). This thermal desorption-mass spectrometry (TOA-QMS) technique is able to acquire particulate organics, sulfate, nitrate, and ammonium mass concentrations, as well as the ratios of oxygen (O), hydrogen (H), and nitrogen (N) to carbon (C), i.e., O/C, H/C, and N/C, as well as the ratio of organic matter (OM) to organic carbon (OC) in a single analysis. The analysis is conducted on archived quartz-fiber filter samples, which can cover large spatial and temporal scales. This thesis first describes the experimental setup, optimization, and calibration. Next, development of fragmentation table and characterization of ionization efficiency are documented. Finally, results of applying this technique to analyze real-world ambient samples are presented. The TD-MS technique is validated by comparing ion chromatography and thermal/optical carbon analyses for wintertime samples collected at Fresno, CA from December 2000 to February 2001.
Dedication

Gostaria de dedicar esta dissertação aos meus pais, Renato Riggio Júnior e Márcia Regina Mazza Riggio, e ao meu irmão, Renato Riggio Neto por sempre estarem ao meu lado e sempre me apoiarem em todas as decisões que tomo. Sem eles tenho certeza de que não estaria aonde estou. Obrigado por tudo.

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Chapter 1: Introduction

1.1 Background

Aerosols, liquid or solid particles suspended in air, represent one of the greatest sources of uncertainties in estimating global climate changes. Atmospheric aerosols scatter and absorb solar radiation, thereby modifying the atmosphere’s radiative properties (IPCC, 2013). They also affect cloud formation, air quality, visibility, as well as ecosystems, and human health (Pope et al., 2009; Watson, 2002a). Large spatial and temporal variations in aerosol concentration, chemical composition, and optical properties (i.e., scattering and absorption) coupled with limited representations of sources and sinks, transport, transformation, and aerosol-cloud interaction result in large uncertainties in climate model calculations (Dubovik et al., 2002; Forster et al., 2007; Haywood and Boucher, 2000).

Exposure to aerosol particles (also known as particulate matter [PM]) has been linked from mild to severe adverse health effects, including chronic cardiovascular and respiratory diseases (e.g., coughing, painful breathing, asthma attacks, heart attacks, bronchitis, decrease lung function, and lung cancer), premature births, premature death, low birth weight, reduced lung growth rate, and decrease in life expectancy (Brauer et al., 2012; Chow et al., 2006a; 2006b; Mauderly and Chow, 2008; Pope et al., 2002; 2004; 2009; Rucker et al., 2011; Sacks et al., 2011; Schwartz, 1993). While most studies have focused on the effects of increase PM in human health, the benefits of PM
reduction have also been studied. Clancy et al. (2002) shows that the ban in coal sales in Ireland reduced black smoke concentration by 35.6 µg/m³ over the following 6 years, while at the same time reducing cardiovascular and respiratory disease related mortality by 10.3% and 15.5%, respectively. An extension of the “Harvard Six Cities study” found a 10 µg/m³ decrease in PM$_{2.5}$ when residents relocated from high to low PM environment resulted in a 27% decrease in overall mortality (Laden et al., 2006).

Aerosols are emitted into the atmosphere through natural and anthropogenic mechanisms by either direct emissions into the air or as a conversion from gaseous precursors (Atkinson et al., 2010). Natural sources include volcanoes, wild fires, dust, and sea spray, while anthropogenic sources include combustion processes from industrial facilities and vehicles, cooking and residential wood burning, agricultural practices, and road dust (WHO, 2014).

Aerosol particles are composed of a complex mixture of inorganic and organic species, including: nitrates (NO$_3^-$), sulfates (SO$_4^{2-}$), ammonium (NH$_4^+$), organic compound (e.g., polycyclic aromatic hydrocarbons [PAHs]), elemental carbon (EC; also known as black carbon, light absorbing carbon, or soot), biological compounds (e.g., endotoxins), metals (e.g., nickel, copper, and zinc), and crustal species (e.g., aluminum, silicon, calcium, and iron) (Chow, 1995; WHO, 2014).

The chemical composition of aerosols highly depends on their origin and location. Aerosols can chemically evolve through oxidation, photo-dissociation, and reactions
with other aerosols or gases, making it a complex system. The situation is especially complicated in urban areas where gaseous and particle emissions from different pollution sources can quickly interact with each other to produce complex compound mixtures. The formation of haze or smog, which reduces visibility, is one of the most clear indications of high concentration of PM in the air (Chow et al., 2002a; Watson, 2002a; 2002b).

The concentration of PM in the atmosphere is an important contributing factor to health and life quality since ultrafine and fine particles can penetrate down to the alveoli and cause several adverse health effects (Chow et al., 2006a, 2006b; Pope and Dockery, 2006). As a result, PM is listed as one of the six criteria pollutants along with carbon monoxide (CO), ozone (O₃), nitrogen oxides (NOₓ), sulfur dioxide (SO₂), and lead. These pollutants are regulated by the National Ambient Air Quality Standards (NAAQS) by the U.S. Environmental Protection Agency (U.S. EPA) as well as environmental agencies in other countries (Cao et al., 2013; EPA, 2006).

Accurate measurement of PM mass concentration and chemical composition are required to demonstrate compliance, assess source contributions, evaluate their air quality, health, and climate impacts, and develop control policies. The Desert Research Institute (DRI) model 2001 thermal/optical carbon analyzer (TOA) is a widely known and proven method used to quantify organic carbon (OC) and EC concentrations. This method has been applied to U.S. long-term urban and nonurban PM monitoring networks (Chow et al., 2007a; 2007b; 2011). In this study, a thermal desorption mass
spectrometry (TOA-QMS) technique was developed to quantify particulate sulfate, nitrate, and ammonium mass concentrations, the ratios of oxygen (O), hydrogen (H), and nitrogen (N) to carbon (C), i.e., O/C, H/C, and N/C, as well as the ratio of organic matter (OM) OC. This method innovatively combines a modified DRI Model 2001 TOA with an electron impaction ionization-quadrupole mass spectrometer (EI-QMS) to fully utilize and expand their capabilities.

1.3 Chemical Characteristics of Aerosols

Atmospheric aerosols are generally classified as either primary or secondary depending on their source or origin. Primary aerosols are emitted directly into the atmosphere from natural and anthropogenic sources, while secondary aerosols are formed in the atmosphere through gas-to-particle conversion from nucleation of gaseous precursors. Secondary aerosol formation has been observed to occur globally and can contribute to the majority of fine particle mass concentrations in polluted areas.

The mass fraction of aerosol chemical components is dependent on climatic conditions, sources, and sampling locations (Wei et al., 2015) shows aerosol composition measured at different sites throughout the northern hemisphere. Pie charts show the average mass concentration and chemical composition of non-refractory PM$_1$ (particles with aerodynamic diameter less than 1 micrometer [µm]) measured with aerosol mass spectrometry. Although EC contribution was not reported,
it is apparent that organics (in green) and sulfate (in red) account for a majority of the PM mass (Zhang et al., 2007). The sum of major inorganic species (i.e., sulfate, nitrate, and ammonium) may account for approximately 30% - 70% of the urban aerosol particles (Zhang et al., 2007).

![Aerosol composition measured at different locations in the northern hemisphere with Aerosol Mass Spectrometers (AMS). Pie charts show the average mass concentration and chemical composition [organics: green, sulfate: red, nitrate: blue, ammonium: orange, chloride: purple]. Black and blue labels indicate urban areas. Pink labels indicate rural areas (Zhang et al., 2007). Elemental carbon was not measured by AMS.](image)

Inorganic ions (e.g., $SO_4^{2-}$, $NO_3^-$, $NH_4^+$) and secondary organic aerosols (SOA) are formed mainly from the gas-to-particle transformation in the atmosphere. The gas-to-particle conversion usually starts when precursor gases such as nitrogen oxide (NO), nitrogen dioxide ($NO_2$), sulfur oxides ($SO_x$), later oxidized to $SO_2$, and volatile organic
compounds (VOC) are released into the atmosphere and react with hydroxyl radical (OH), oxygen (O₂), or O₃. The product of these reactions usually yields the formation of secondary aerosols (Pitts-Finlayson and Pitts Jr., 2000).

Gaseous SO₂ can be oxidized in both the gaseous and aqueous phase. The mechanism for gaseous phase oxidation can be seen in reactions R1-R3 below, where SO₂ oxidation yields sulfuric acid (H₂SO₄). The yield of H₂SO₄ requires a third body M in equation R1, which could be any molecule present in the air, in order to maintain the conservation of momentum. Reactions R2 and R3 are so fast that are mostly dependent on the concentration of OH (Gleason et al., 1987).

\[
\begin{align*}
SO₂ + OH + M & \rightarrow HSO₃ + M \quad (R1) \\
HSO₃ + O₂ & \rightarrow HO₂ + SO₃ \quad (R2) \\
SO₃ + H₂O & \rightarrow H₂SO₄ \quad (R3)
\end{align*}
\]

When clouds are present, the loss rate of SO₂ is faster than it can be explained by the gas phase oxidation mechanism alone. This is due to reactions in the liquid water droplets. Research has shown that most of the atmospheric oxidation of SO₂ takes place in cloud and rain drops, where SO₂ is converted to hydrogen sulfite (HSO₃), which is then oxidized by peroxide (H₂O₂) produced from hydroperoxyl (HO₂) self-reaction (Burkhard et al., 1994). The size of SO₄²⁻ particle formed after cloud water evaporation is usually dependent on the amount of SO₂ dissolved. Sulfate particles are hygroscopic and can take up significant amounts of water vapor and produce much larger particles compared
to its dry mass (Martin, 2000). The $\text{SO}_4^{2-}$ particle formed after water evaporation is usually in the accumulation mode. Reactions R4-R6 below show the formation of particulate $\text{SO}_4^{2-}$ from the reaction of $\text{SO}_2$ with water (Hegg and Hobbs, 1978):

\[
\text{SO}_2(g) \rightarrow \text{SO}_2 \cdot \text{H}_2\text{O} \tag{R4}
\]

\[
\text{SO}_2 \cdot \text{H}_2\text{O} \rightarrow \text{HSO}_3^- + \text{H}^+ \tag{R5}
\]

\[
\text{HSO}_3^- + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O} \tag{R6}
\]

In continental aerosols, $\text{NH}_4^+$ is the main cation associated with sulfates even though it can rapidly react with nitric acids (HNO$_3$) to form particulate ammonium nitrate ($\text{NH}_4\text{NO}_3$). Such is the case because the reaction between ammonia (NH$_3$) and H$_2$SO$_4$ is favored over the reaction of NH$_3$ with HNO$_3$. Reactions R7 – R8 below shows the reaction of NH$_3$ with H$_2$SO$_4$ for the formation of ammonium bisulfate ($\text{NH}_4\text{HSO}_4$) and/or ammonium sulfate ($\left(\text{NH}_4\right)_2\text{SO}_4$) (Scott and Cattell, 1979).

\[
\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NH}_4\text{HSO}_4 \tag{R7}
\]

\[
\text{NH}_4\text{HSO}_4 + \text{NH}_3 \rightarrow \left(\text{NH}_4\right)_2\text{SO}_4 \tag{R8}
\]

In the atmosphere, mixture of $\text{NH}_4^+$ and NH$_3$ (NH$_x$) returns to the surface as either gaseous or particle phase. The quantification of atmospheric NH$_3$ is challenging since NH$_3$ is a sticky gas and adsorbs onto almost all surfaces. However, much of the surface adsorbed NH$_3$ will desorb if concentration levels decrease in the air stream. Such process can create positive and negative artifacts in sampling and analytical systems and
cause large measurement uncertainties. In the U.S. for example, and NH₃ emissions inventory is highly uncertain and little is known about the dry deposition process (NOAA, 2000; Sheppard et al., 2011)

Significant levels of NH₄NO₃ are formed where SO₄²⁻ concentration/ emissions are low and NH₃ and NOₓ emissions are high (e.g., Southern California and the Mountain West). Its formation also largely depends on the thermodynamic state of its precursor and on environmental conditions. Particulate NO₃⁻ formation is enhanced at night time, when atmospheric NH₃ is in excess and temperature is lower (Chen et al., 2012).

Reactions R10 – R11 below describes the formation of NH₄NO₃ in the atmosphere (Pitts-Finlayson and Pitts Jr., 2000; Seinfeld and Pandis, 2006).

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + O_2 & \text{(R10)} \\
\text{NH}_3 + \text{NO}_2 + \text{OH} + \text{M} & \rightarrow \text{NH}_4\text{NO}_3 + \text{M} & \text{(R11)}
\end{align*}
\]

or

\[
\begin{align*}
\text{NO}_3 + \text{NO}_2 + \text{M} & \rightarrow \text{N}_2\text{O}_5 + \text{M} & \text{(R12)} \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 & \text{(R13)} \\
\text{NH}_3(g) + \text{HNO}_3(g) & \leftrightarrow \text{NH}_4\text{NO}_3 & \text{(R14)}
\end{align*}
\]

The low saturation vapor pressure of H₂SO₄ plays an important role in the formation of NH₄NO₃. Since (NH₄)₂SO₄ is the preferred form of SO₄²⁻ (i.e. one mole of of SO₄²⁻ will remove 2 moles of NH₃ from the gas phase), two regimes are important for nitrate aerosol formation: 1) NH₃ rich and, 2) NH₃ poor (Bauer et al., 2007). In the ammonia-rich regime, excess NH₃ in the aerosol phase is able to neutralize most sulfates. The NH₃ that
does not react with $\text{SO}_4^{2-}$ will then be available to react with nitrate to form $\text{NH}_4\text{NO}_3$ (Bauer et al., 2007). In the NH$_3$ poor regime, sulfates will not be completely neutralized and the aerosol phase will be acidic. In addition, $(\text{NH}_4)_2\text{SO}_4$ is more stable than $\text{NH}_4\text{NO}_3$. Depending on ambient temperature and relative humidity, volatilization of $\text{NH}_4\text{NO}_3$ occurs (Watson et al., 1994). With low vapor pressure, the NH$_3$-HNO$_3$ reaction partial pressure will be low and the $\text{NH}_4\text{NO}_3$ concentration will be low or zero (Bauer et al., 2007).

Aerosol NO$_3^-$ is not only associated with NH$_3$ however. Mineral dust and sea salt for example have an important impact on NO$_3^-$ formation as well. Lefer and Talbor (2001) found that 86% of NO$_3^-$ mass in an acidic environment had particle diameter (Dp) larger than 1 µm, indicating its association with minerals. Once HNO$_3$ is formed for example, it is likely to react with salt (e.g., NaCl) and produce NaNO$_3$ (Chow et al., 2015b). The presence of Mg$^{2+}$, Ca$^{2+}$, and K$^+$ can also result in aerosol NO$_3^-$ formation (Lefer and Talbot, 2001).

Unlike inorganic species, organic aerosols cover a wide range of molecular forms and are one of the most abundant species in PM$_{2.5}$ (particles with aerodynamic diameter less than 2.5 µm). They consist of volatile, semi-volatile, and non-volatile components (Donahue et al., 2009; 2013). VOCs, or high vapor pressure compounds, include short-chain alkanes, are always in the gas phase, and are the key precursors in the chemical reactions to form tropospheric O$_3$. Semi-volatile organic compounds on the other hand, are larger compounds and can either be in particulate phase by themselves or condense
onto the surfaces of other aerosols. Non-volatile organics do not readily vaporize (Jacobson et al., 2000). Particulate OC is then composed of the particulate fraction of the semi-volatile and non-volatile organics. In most cases, primary OC dominates over secondary OC. However, during peak photochemical air pollution episodes, secondary OC may exceed primary OC (Jacobson et al., 2000).

The most effective oxidants of organic aerosols include $O_3$, hydroxyl (OH), and $NO_3$ radicals. These oxidizers are produced photochemically and are active during limited times of the day. In order for SOAs to form, high concentrations of the product between the oxidizer and the organic compounds must exist. If the organic compound is reactive, it becomes smaller and more polar through oxidative cleavage and the addition of $O_2$. If these compounds become associated with cloud droplets, aqueous phase reactions can change the chemical composition of the organic material and form new organic. Several studies have shown that the most abundant dicarboxylic acids in the atmosphere are oxalic acid, followed by malonic acid, and succinic acid. Oxalic acid, a by-product of fossil fuel combustion, biomass burning, and biogenic activity, has shown by many studies to be the most abundant dicarboxylic acid in tropospheric aerosol, will be further discussed in later chapters (Kawamura and Ikushima, 1993; Kawamura and Kaplan, 1987; Kawamura et al., 2003; Loflund et al., 2002). To put into perspective, oxalic acid’s abundance in the atmosphere accounts for more than 80% of the diacids found in the in the relatively clean Arctic regions (Kawamura et al., 1995). Hence its concentration levels observed in these regions can be used as a measurement for background levels.
PAHs are also a group of organic compounds of great interest due to their carcinogenic and mutagenic characteristics. They also serve as markers for different aerosol sources, e.g., retene for wood combustion, benzo(ghi)perylene and indeno[123-cd]pyrene for gasoline, and ratios of fluorene to pyrene for splitting gasoline and diesel emissions (Chow et al., 2007b; 2007c; Tobiszewski and Namiesnik, 2012).

1.4 Aerosol Chemical Composition Measurement Techniques

While counting and sizing aerosols may be relatively easily done with a differential mobility analyzer (DMA) and condensation particle counter (CPC), measuring the chemical composition of aerosols is more complicated. Atmospheric aerosols can contain hundreds of compounds with wide range of chemical and thermodynamic properties. Both on-line and off-line methods have been used to analyze aerosol components in elemental or molecular levels (Chow et al., 2007b; 2007c; 2008a; McMurry, 2000; Noble and Prather, 2000).

1.4.1 On-line Methods

On-line methods involve in-situ measurements of the aerosol chemical composition. These methods have great potential to reduce particle volatilization by eliminating the need for sample transport and storage. The automation of on-line techniques reduces operator time and costs, and provides higher time-resolution to understand temporal variation of aerosol emissions and evolution. However, the resources are focused at specific sampling locations requiring great effort in data processing, data validation, and
data interpretation. Examples of on-line aerosol chemical characterization include: the aethalometer (Hansen et al., 1984), flame photometric detectors (FPD) (Brody and Chaney, 1966), particle into liquid sampler (PILS) (Sorooshian et al., 2006a), monitor for aerosol and gas in ambient air (MARGA) (ten Brink et al., 2007), ambient ion monitor (AIM) (URG Corp. Chapel Hill, NC), and the aerosol mass spectrometer (AMS) (Jayne et al., 2000). A more comprehensive list of methods was described by Chow et al. (2008).

The aethalometer estimates concentration of black carbon (BC) in the sampled air based on filter sample light attenuation (Hansen et al., 1984). The relationship between light attenuation and BC is affected by the filter matrix, non-light absorbing aerosol, and filter loading, and various algorithms have been developed to account for these artifacts. Instruments that operate on a similar principle include de particle soot/absorption photometer (PSAP) (Radiance Research, Seattle, WA) and the multiangle absorption photometer (MAAP) (Petzold and Schönlinner, 2004).

The flame photometric detector (FPD) was developed to measure particulate sulfate concentration in the atmosphere by detecting the light given off by excited-state electrons when sulfur (S) compounds are combusted in a hydrogen (H) rich flame. This method does not distinguish between particulate and gas phase S and a denuder is often necessary to remove the gaseous fraction (Huntzicker et al., 1978). A technique to measure NO$_3^-$ was developed using the FPD and a NO$_x$ gas analyzer (Stolzenburg and Hering, 2000).
The particle into liquid sampler (PILS) measures several ions in PM by utilizing the general principles of ion chromatography (IC). In short, ambient particles are grown in a water vapor saturated environment and are collected on a surface that is continually flushed with water. The liquid sample is then injected into a dual-channel system for the analysis of cations and anions (Weber et al., 2001).

The aerosol mass spectrometry (AMS), one of the techniques in the apportionment of atmospheric aerosols particles, measures the aerosol size and chemical composition in situ (Canagaratna et al., 2007, 2015; DeCarlo et al., 2006; Gard et al., 1997; Jayne et al., 2000; Jimenez et al., 2003; Johnston, 2000; Nash et al., 2006; Noble and Prather, 1999, 2000; Oktem et al., 2004; Prather et al., 1994; Spencer and Prather, 2006; Wexler and Johnston, 2001a). The conventional Aerodyne AMS works by drawing ambient aerosols through an aerodynamic lens inlet and focusing them into a collimated beam. The particles then impact onto a tungsten surface heated to ~450 °C - 650 °C and flash vaporize. Vaporized species are ionized and analyzed by a mass spectrometer. It usually provides mass concentration in µg/m³ of particulate NO₃⁻, SO₄²⁻, NH₄⁺, OM, and non-sea salt chloride. It is not able to detect EC, sea salt, or dust. Several different types of mass spectrometers have been employed, including quadrupole, time-of-flight, ion trap, and magnetic sector instruments (Liu et al., 1995a; Wang and McMurry, 2006). Several different types of mass spectrometers have been employed, including quadrupole, time-of-flight, ion trap, and magnetic sector instruments. Recently, a Single Particle Soot Photometer (SP2) (Stephens et al., 2003) was added to the Aerodyne AMS to enable
measuring fractal soot particles (Onash et al., 2012). The Aerodyne AMS measures ensemble particles, while several types of AMS, e.g., the Aerosol Time-of-Flight Mass Spectrometry (ATOFMS) measures the chemical composition of individual particles. Reviews of AMS can be found in several publications (Noble and Prather, 2000; Wexler and Johnston, 2011).

1.4.2 Off-line Methods

Measurements of particle chemical composition using offline methods involve collecting particles on substrates for a defined period of time and flow rate and transporting the samples into the laboratory for extraction and analysis. Sampling duration varies depending on environmental conditions and financial resources, but is usually done in 24 hours (midnight to midnight) to represent human exposure to ambient pollutants. Chow et al. (2008) provides a comprehensive review on off-line measurements methods.

Collection of particles onto filter substrates is the most common method for determining PM composition. In addition to chemical information, off-line methods can also discriminate between particle size when using a cyclone separator or a cascade impactor. Separation of aerosol by size makes it especially useful for health effect studies.

Impaction surfaces are another variable in off-line measurements. In general, particle sampling filter substrates consist of tightly woven fibrous mat, or a plastic membrane penetrated by microscopic pores Teflon membrane filters are often used for
gravimetric mass analysis, whereas quartz-fiber filters are used for OC/EC and ion composition analyses. Although pre-fired quartz-fiber filters are necessary before field sampling to remove organic artifacts, the evolution of analysis technique has made such task trivial. Quartz-fiber filters are often used for destructive type analytical methods, while Teflon-membrane filters are suitable for non-destructive analysis.

Filters should have >99.7% collection efficiency at the specified sampling flow rate (U.S.EPA, 1997). In addition, the filter material should not react with the collected particles as to prevent interference in the follow up chemical analysis. Adsorption of SO$_2$, NO$_x$, and water vapor has been identified as potential interferences with chemical measurements. However, the uses of non-acidic and non-alkaline filters are able to eliminate majority of these artifacts. The absorption of organic gases by quartz-fiber filters is still an interference to chemical measurements and may cause a positive bias in measurements (Chow, 1995, 2015a; Turpin et al., 1994). Nonetheless, as sample duration increases, the adsorption bias is reduced as adsorbed gases reach equilibrium with the collected particles and the filter becomes saturated (Chow, 1995).

Present analytical methods for the analysis of organic and inorganic aerosols are largely based on solvent extraction of quartz-fiber and/or Teflon–membrane filters using water and/or organic solvents prior to thermochemical and chromatography analyses; these procedures are costly and require lengthy derivatization reactions (Chow et al., 2008; Grosjean, 1975; Novakov and Corrigan, 1995). A few off-line techniques include: atomic absorption spectroscopy (AAS), high performance liquid chromatography (HPLC),
gas chromatography (GC), scanning electron microscopy (SEM), nuclear magnetic resonance (NMR), secondary ion mass spectrometry (SIMS), X-ray fluorescence analysis (XRF), IC, inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Chow, 1995; McMurry, 2000).

Thermal desorption technique is one of the few types of analysis that do not require solvent extraction. Thermal/optical carbon analysis focus on releasing carbonaceous material from particle-laden quartz-fiber filters at different temperatures (Chow, 1993; 1995; 2007b) and is the one on which this research is based on.

1.5 Research Overview

This study couples a DRI Model 2001 thermal/optical carbon analyzer is coupled to an electron ionization-quadrupole mass spectrometer (EI-QMS) to be used as a TOA-QMS setup for quantification of inorganic and organic aerosol species collected on quartz-fiber filters. Quantified species include organics, NO$_3^-$, SO$_4^{2-}$, and NH$_4^+$ species. Since the analysis is conducted on quartz-fiber filters, samples collected over wide spatial and temporal scales, including those collected in many national networks (e.g., IMPROVE and CSN) can be analyzed to obtain additional information. Filters can be archived for additional analyses if necessary. The TOA-QMS multidimensional capability removes the need for analysis of the same filter by different techniques, which lowers analysis costs by reducing sample manipulation and analysis time. It also reduces analysis uncertainties since these analyses are conducted on the same filter material by
the same setup. The filter-based TOA-QMS is a complement to the more expensive online AMS.

This research involved the following steps: 1) design and optimization of the TOA-QMS system; 2) development of calibration curves and fragmentation table; 3) development of efficient data analysis methods; 4) validation of the TOA-QMS with established methods (i.e., TOA for carbon and IC for ions); 5) using the TOA-QMS to analyze source and ambient samples. A total of 104 PM$_{2.5}$ ambient filters, including replicates were analyzed. These filters include winter, spring, and summer samples from the Fresno Supersite, as well as 11 samples from Baltimore, MD.
Chapter 2: Methodology

2.1 Instrument Description

A DRI Model 2001 Thermal/Optical Carbon Analyzer (Chow et al., 1993; 1995; 2001; 2004; 2005; 2007a, 2011) was modified to enable the thermal desorption/mass spectrometry (TOA-QMS) analysis of aerosol-laden quartz-fiber filter samples (Figure 2-1). The DRI carbon analyzer has been extensively used for measurement of OC and EC in source and ambient aerosol samples (Li et al., 2007; Maykut et al., 2003; Subramanian et al., 2006). This technique is based on the preferential oxidation of OC and EC materials under different temperatures and atmospheres.

Figure 2-1. The TOA-QMS setup coupling a Thermal Optical Carbon Analyzer with a Quadrupole Mass Spectrometer.

In an unmodified DRI Model 2001 TOA, a ~0.5 cm² punch from a particle-laden quartz-fiber filter is heated in a sample furnace following a pre-specified temperature protocol, first in inert pure He atmosphere at lower temperatures, and later in an
oxidizing atmosphere with 98% He and 2% O₂ at higher temperatures. The thermally-evolved gaseous products are passed through a manganese dioxide (MnO₂) oxidation reactor, yielding mainly CO₂ and CO products, and follow by reducing to methane (CH₄) by hydrogen (H₂) on a nickel catalyst. The CH₄ is quantified using a flame ionization detector (FID). Detailed information regarding the working principle and operation procedures of the DRI TOA can be found in Chow et al. (1993; 2007b; 2011).

Efforts have been made to modify the DRI Model 2001 TOA to acquire more chemical information from a single quartz-fiber filter punch (Robles et al., 2013; Wang et al., 2011; Yang et al., 2013) including a recent effort that hyphenated a carbon analyzer with a photo-ionization time-of-flight mass spectrometer (PI-TOF-MS) to detect the organic composition of PM collected on quartz-fiber filters (Diab et al., 2015; Grawbosky et al., 2011).

The schematic of the modified analyzer is shown in Figure 2-2. Although the ultimate goal is to conduct carbon and EI-QMS analysis simultaneously on the same instrument, no carbon analysis components (i.e., MnO₂ reactor, Ni reactor, and FID) were included in the current setup in order to eliminate any possible interference of the MnO₂ reactor with the analysis.

The TOA-QMS uses the same sample oven as an unmodified DRI Model 2001 TOA. Thermally-evolved gas products from the quartz-fiber filter are passed through a thermal fragmentation oven (an empty quartz-glass tube) heated to 650 °C. This
temperature was selected based on two factors: (1) preliminary experiments showed that a temperature greater than 550 °C is necessary to achieve good transfer efficiency, and (2) the vaporization temperature employed by the Aerodyne El-AMS is typically ~450 - 650 °C (Canagaratna et al., 2007; Jayne et al., 2000; Jimenez et al., 2003). At such temperature, organic compounds with high molecular weight are broken down (often with low volatility) into small fragments, thereby reducing condensation loss.

Figure 2-2. Schematic of the TOA-QMS system for PM$_{2.5}$ organic and inorganic measurement. A particle-laden quartz-fiber filter punch is introduced into the oven by a pushrod and heated in preprogrammed steps. Thermally desorbed molecules are carried by a helium gas at 50 mL/min flow rate to a heated thermal fragmentation oven at 650 °C, where larger molecules are thermally broken down to smaller fragments to prevent condensation in the transfer line downstream. The resultant species are transferred through a deactivated fused silica capillary heated at 220 °C to an electron-ionization quadrupole mass spectrometer (EI-QMS). An argon sheath at the interface of the pushrod and oven prevents intrusion of ambient gases into the instrument. An aliquot of 5 mL CO$_2$ is introduced at the end of the analysis as a calibration standard. The downstream end of the thermal fragmentation oven is connected through a 1/16” (OD) × 1” (length) stainless steel tube via a Swagelok (Swagelok, Solon, OH) adapter to a
Valco (Valco Instruments Co. Inc., Houston, TX) microvolume connector. The gas stream is split into a 48 mL/min to a vent via a 1/16” (OD) × 6” (length) stainless steel tube followed by a needle valve and ~2 mL/min to an EI-QMS (Agilent MSD 5975; Agilent Technologies, Santa Clara, CA) via a Valco micro-metering valve and a deactivated quartz capillary (200 µm ID; Agilent Technologies, Santa Clara, CA, USA). To minimize condensation loss, the Swagelok adapter, the microvolume connector, and the micro-metering valve are enclosed within a custom-made heated box heated at 210 °C by two 65W cartridges at the bottom. The deactivated capillary is enclosed in a heated transfer line (220 °C) that connects the heated box to the mass spectrometer inlet (heated to 230 °C). According to Grabowsky et al. (2011), this differential heating effectively reduces the condensation of low-volatility compounds along the capillary and at the mass spectrometer inlet. Figures A-1 and A2 in Appendix A show the argon sheath design and specifications. Appendix E shows a list of parts necessary to modify the TOA into a TOA-QMS.

A back pressure regulating valve is used to regulate the gas pressure in the oven to ~10 psi (69 kPa). Maintaining a relative high sample chamber pressure reduces air intrusion (primarily via diffusion) into the system since trace O₂ may react with desorbed organic compounds and reduce MS detection sensitivity. The flow rate and pressure of the He carrier gas and argon (Ar) gas sheath are separately controlled by two mass flow controllers (Alicat Scientific, Tucson, AZ) and two pressure gauges.
The temperature setting for the EI-QMS is 230 °C for the ion source and 150 °C for the MS. The EI-QMS was configured via the Agilent ChemStation software to collect a mass spectrum from 10 to 450 Da every 1.2 second. The instrument is purged for 5 minutes with ultrapure He gas and tuned with the mass spectrometer’s internal solution of perfluorotributylamine every day before analysis in order to maximize sensitivity. Tuning is done automatically by Agilent’s standards.

Chemical identification of desorbed molecules is made at three temperature steps (80 °C, 580 °C, and 840 °C) lasting 10 minutes each. The purpose of each temperature steps are as follows: 1) remove water and other high VOCs from the system (80 °C); 2) desorb and pyrolyze aerosol constituents present on the filter punch (580 °C) and, 3) desorb excess species that remain in the quartz-fiber filter punch that are not desorbed at the previous steps, or that are trapped on the walls of the system (840 °C). The temperatures of 580 °C and 840 °C coincide with the IMPROVE_A protocol temperatures for OC4 and EC3 (Chow et al., 2007a) to facilitate comparison with OC/EC analyses. Since a He/O_2 mixture is not introduced into the system for EC to be measured, signals obtained at 580 °C represent the same total organic carbon fraction observed using DRI’s model 2001 TOA running the IMPROVE_A temperature protocol. Only three steps are used in this study to obtain high MS signal. Future study will explore using all steps in the IMPROVE_A for the TOA-QMS analysis. The temperature of the system was calibrated using a NIST certified thermocouple at several different temperatures. An example of temperature calibration can be seen in Figure A- in appendix A.
A 5% CO₂/He mixed gas is injected as an internal standard using a Carle valve at the end of each run. The use of CO₂ as the internal standard, instead of CH₄ (the original DRI TOA internal standard gas) removes the uncertainty generated by the overlapping fragmentation signals of O₂ (m/z=16 for O⁺) and CH₄ (m/z=16 for CH₄⁺). Unit mass resolution data is used to quantify organic compounds, SO₄²⁻, NO₃⁻, and NH₄⁺, similar to that obtained from an AMS (Aiken et al., 2007; Allan et al., 2004; Jimenez et al., 2003).

Figure 2-3. Thermogram of a Birch log burning emission sample collected on a quartz-fiber filter overlaid with its chromatogram and IMPROVE_A temperature protocol. Most of the signal is observed at 580 °C. Integration of the peaks closely match OC data obtained with DRI’s model 2001 TOA running the IMPROVE_A temperature protocol.

The typical analysis results in two major components: a chromatogram as a function of the temperature protocol and a mass spectrum. Chromatogram analysis indicates that the majority of aerosol desorption from the media occurs at 580 °C and 840 °C.
(Figure 2-3). As a result, ions measured at these steps constitute the majority of the signal observed, and are added to represent the total aerosol deposited on the quartz-fiber filter. Signals observed at 80 °C are also added to the total signal to form a complete depiction of the aerosol desorbed from the media.

2.2 Instrument Optimization

Optimization of the TOA-QMS is important in order to obtain consistent mass spectra and reduce chemical interferences. The main component to achieve consistent analysis requires regulating the pressure of the system, the pressure of the argon sheath, and regularly cleaning the mass spectrometer parts and changing the ion source. In conjunction, these measures considerably reduce ambient intrusion and minimize oxidation of the particles, and optimize the sensitivity of mass spectrometer.

The first step to suppress air intrusion and reduce O₂ concentration in the TOA-QMS was to increase the sample oven pressure from ~5 psi in the DRI Model 2001 carbon analyzer to 10 psi in the TOA-QMS. The 10 psi value was selected to reduce air intrusion while keeping the breach of the TOA sealed. Pressures higher than 10 psi will push the breach slightly open and a loss of the carrier gas and pressure in the system can be detected. A reduction of 70.51% in the O₂ signal was observed from 0.83 psi to 10 psi, and reduction of 40.44% is observed from 5.85 psi to 10 psi. The pressure of the system must be sufficient to avoid intrusion but not affect the entry port. Figure 2-4 shows the effects of sample oven pressure on measured oxygen content. The O₂ (m/z = 32)
baseline intensity reduced from 0.74 at 0.83 psi to 0.22 at 10 psi. A percent change of 70.5%

Improvements to ambient intrusion were then investigated and the TOA-QMS was checked for other means of intrusion. Two other possible pathways were investigated: 1) the carrier gas, and 2) the Teflon and Swagelok connections.

In order to avoid contamination by the carrier gas, especially by ambient O₂ or cylinder contaminants, installation of a gas purification system containing two high volume O₂ scrubbers (Restek Corporation, Bellefonte, PA, part #20601), capable of reducing O₂ to 15 ppb by neutralizing it, and two indicating O₂ scrubbers (Restek, Corporation, Bellefonte, PA, part #22010) capable of reducing O₂ to 0.1 ppm, were installed upstream of the He flow before introduction to the TOA. High volume scrubbers are alternated with the indicating scrubbers. According to the manufacture specifications the high volume O₂ scrubber purifies more than five 200 ft³ cylinders, while the indicating O₂ scrubber changes from light green to grey when its adsorption capacity is depleted.

Ambient intrusion through connections was investigated by spraying 1,1,2,2 tetrafluoroethane (C₂H₂F₄) trace gas at the TOA-QMS connections. The signal of ion m/z = 83 (C₂H₂F₃) was monitored by the MS. Figure 2-5 illustrates an example of m/z=83 signal when different connections were sprayed at. It was found that ambient intrusion occurred through most of the connections. The largest source of ambient intrusion was
observed at the Teflon ferrule that allows the thermocouple push rod to carry the sample into the oven.

To further reduce ambient air intrusion, an argon sheath chamber that surrounds the sample entry port was designed, manufactured, and installed. To reduce the cost, argon (Ar) instead of He was used as the sheath gas. The argon sheath chamber moves in synchrony with the entry port while still allowing for the thermocouple push rod to move freely. Figure 2-6 shows the position of the argon sheath chamber on the TOA-QMS.

![System Pressure vs. Oxygen Signal](image)

Figure 2-4. Oxygen baseline signal relationship to the system oven pressure. As the sample oven pressure increases the oxygen baseline signal decreased. This demonstrates that high pressure system is necessary to reduce oxygen ambient intrusion into the TOA-QMS and reduce sample oxidation (Yang, 2013).
Figure 2-5. TOA-QMS intrusion testing chromatogram. The chromatogram of m/z = 83 was monitored while different connecting parts were sprayed with 1,1,2,2-tetrafluoroethane (C₂H₂F₄). The largest source of ambient intrusion is the Teflon ferrule that allows the thermocouple rod to carry the sample into the oven. X2 indicates that the two peaks are a response to spraying the connections two times.

Figure 2-6. Photograph of the argon sheath chamber. It reduces ambient air intrusion and considerably reduces the amount of oxygen into the system so that oxidation of desorbed aerosol species is reduced.

The pressure of the argon gas sheath chamber is controlled independently of system pressure. To optimize this pressure, the ambient air and argon ion signals (m/z = 28, 32, and 40) were monitored by the MS while varying the sheath chamber pressure. Figure 2-7 shows the effects of the argon sheath in reducing the ions of O₂ (m/z = 32) and CO
(m/z =28) baseline in the system with an increase in the Ar sheath chamber pressure, while maintaining the TOA-QMS pressure at 10 psi. Ar intrusion into the TOA-QMS was monitored from the Ar ion (m/z = 40). The Ar ion signal (m/z=40) was low and did not change much with increasing the pressure of the Ar chamber. On the other hand, the abundance of the ions at m/z 28 and m/z 32 were reduced with an increase in chamber pressure, and the reduction increased with increasing the sheath chamber pressure. However, the ion signal reduction from 6.5 psi to 7 psi is low. Further increasing the pressure would cause Ar intrusion into the analyzer and waste of Ar gas. Therefore, the 7 psi sheath pressure is deemed as optimal.

Figure 2-7. Effects of the argon sheath chamber pressure on mass spectra signal abundance for CO (m/z 28), O₂ (m/z 32), and Ar (m/z 40). As the pressure increased the signal abundance for CO and O₂ decreased, while the signal abundance for argon was maintained fairly constant at an average abundance of ~11,000, and as seen at m/z 40.
The O\textsubscript{2} in the TOA-QMS was further measured by gas-chromatography/mass spectrometry (GC/MS) analysis. It was found that the amount of O\textsubscript{2} in the system was reduced by 45% from 15.5 ppm to 8.5 ppm, with the addition of the O\textsubscript{2} scrubbers and the Ar sheath chamber, when compared to one that utilized only one oxygen scrubber without Ar sheath chamber, and was held at approximately 5 psi.

One example on how these measures improve sample analysis can be seen for a sample of 16-hydroxyhexadecanoic acid. Figure A- in Appendix A shows example mass spectra comparing when analysis was done with and without the argon sheath chamber. When the argon sheath chamber was not used, a negative peak at m/z 32 (O\textsubscript{2}), a larger peak at 44 m/z (CO\textsubscript{2}), and a smaller peak at 28 m/z (CO) were observed. This observation indicates that the available O\textsubscript{2} present in the TOA-QMS was most likely used to form CO\textsubscript{2} by oxidizing CO. A much larger CO (m/z 28) and non-negative O\textsubscript{2} (m/z 32) peaks were observed when the argon sheath chamber was used.

2.3 Instrument Operation

Operation of the TOA-QMS is very similar to sample analysis with DRI’s model 2001 thermal/optical carbon analyzer (Chow et al., 1993). As the name of the instrument implies, a few modifications are necessary to ensure a reproducible and effective analysis. The two major differences include sample preparation and time synchronization between the carbon analyzer and the mass spectrometer at the start of each run.
Sample preparation involves maintaining particle-laden quartz-fiber filters in a desiccator for up to 24 hours before analysis. Maintaining filters in a low relative humidity (RH; approximately 3% RH) will minimize the interference from water. Adsorption of volatile organic compounds onto the filters while in the desiccator is assume to be negligible since blank filters used for background subtraction go through the same pre-analysis process. Synchronization between the instruments facilitates data analysis and ensures that the custom developed analysis programs developed in MatLab (MATLAB R2014a, The MathWorks Inc., Natick, MA) runs properly. See Appendix B for MatLab program codes and algorithms.

2.3.1 Instrument Startup

Daily startup procedures are followed to reduce background noise and optimize MS performance. In relation to DRI’s model 2001 TOA, the startup cleans the system from molecules that may have adhered to the sample oven, quartz boat, or thermocouple while the instrument was in standby mode at ambient temperature. This is achieved by running the BakeMonitor protocol included in the DRI’s model 2001 TOA software. This protocol increases the sample oven temperature to 840 °C for 30 minutes. In relation to the EI-QMS, startup involves automatic tuning the instrument with its internal perfluorotributylamine (PFTBA) solution for optimal mass-to-charge ratio (m/z) detection. Auto tuning of the EI-QMS is done with the Quick Tune option in the Agilent’s Enhanced Data Analysis software (Agilent Technologies, Santa Clara, CA). The auto tune automatically adjusts the instrument for optimal response.
2.3.2 Sample Analysis Procedure

The following steps are performed in order to successfully analyze particle-laden quartz-fiber filters once sample preparation is complete. Total analysis time is divided into 5 minutes purge, 10 minutes at step 1 (80 °C), 10 minutes at step 2 (580 °C), 10 minutes at step 3 (740 °C), and 5 minutes for the internal calibration to be measured, for a total analysis time of 40 minutes.

DRI’s model 2001 thermal/optical carbon analyzer:

1) Start the DRICarb program and proceed to the analysis subsection.

2) Input the sample information.

3) Select the cmdTDMS3Step protocol that was custom developed for TOA-QMS analysis.

4) Follow the command prompts that appear on the screen and load the sample into the sample boat; ensure that there is a 300 second purging before cmd3Step protocol starts.

5) Start the analysis.

While the DRICarb software is counting down the 300 second purge, proceed to open the Agilent’s Enhanced Data Analysis software and follow the steps:

1) Select the C-TDMS.M method from the Method pull down menu. The C-TDMS.M method was especially developed for the TOA-QMS and works in conjunction with the cmdTDMS3Step protocol.
2) Input the sample information and select the folder in which the run will be saved. It is preferred to input the same sample information as that in the Model 2001 TOA analyzer.

3) Click *OK and Run Method* at the bottom of the window. An acquisition window will pop up and a *Start Run* button will be available. Do not click *Start Run* just yet.

4) Refer back to the DRICarb program and watch as the 300 second countdown approaches 0.

5) When the countdown reaches 0, click the Start Run button on the Agilent’s Enhanced Data Analysis software.

### 2.3.3 Analysis Protocol

The protocol and the method chosen for the TOA-QMS must work in synchrony for the automated data analysis program to function properly. Synchronization is mainly achieved by ensuring the same starting times for DRI’s TOA and the EI-QMS.

The *cmdTDMS3Step* protocol is the main, and most important, protocol in the EI-QTDMS analysis. Its main function is to control the temperature of the DRI’s TOA sample oven, the position of the sample within the analyzer, delay times, and valve positions. The series of events that take place within the protocol once sample analysis starts is explained below.
1) The sample oven temperature is set to 5 °C and the sample oven fan is turned on to cool the sample oven to room temperature. The Carl valve is set to load calibration CO₂ gas.

2) Once the sample oven temperature reaches just below 100 °C, the sample boat moves to the calibrate position and is cooled down further.

3) Once the sample oven temperature is reduced from 100 °C to 55 °C a prompt displays the option to start the next analysis.

4) If the prompt is accepted, the sample boat moves to open position and the analyzer breach is opened.

5) A prompt indicating to load the sample appears. The sample oven fan is turned OFF.

6) Once the sample is loaded, the sample moves to the analyze position and the sample oven fan is turned ON.

7) Once in the analyze position a prompt indicating a 300 second delay appears.

8) Once the 300 second delay expires, data collection begins for 300 seconds and the back valves open to introduce the analysis flow to the MS.

9) After 300 seconds, the sample oven fan is turned off and the temperature is ramped to 80 °C and maintained for 600 seconds (STEP 1).

10) After 600 seconds the temperature is ramped to 580 °C and maintained for another 600 seconds (STEP 2).

11) Finally, the temperature is ramped to 840 °C and maintained for another 600 seconds (STEP 3).
12) At the end of STEP 3, the Carle valve injects calibration gas into the analyzer and data is collected for 150 seconds.

13) The run finishes. The back valves are closed. The sample oven fan in set to ON to cool the oven. A report is created.

While the cmdTDMS3Step is executed by the DRICarb program, the C-TDMS.M method set in Agilent’s software controls the time period during which the mass spectrometer will acquire data, the m/z range, and the time of each scan. Table C- in Appendix C shows the details of the full operation of this custom protocol. Table 2-1 shows the parameters used for the C-TDMS.M method.

Table 2-1. Parameters used in the C-TDMS method found in Agilent’s El-QMS software.

<table>
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<td>MS Quad. Temp. ( °C )</td>
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</tr>
</tbody>
</table>
Chapter 3 : Analysis Techniques

3.1 Quantitative Analysis

The formulation to calculate mass concentrations in the system for organics, $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$ is similar to those used for the Aerodyne AMS described in details by Jimenez et al. (2003). The molecular flux $M_i$ (molecules/s) of a species $i$ entering the TOA-QMS per unit time is calculated from the signal at a single $m/z$ as:

$$M_i = \frac{I_i}{X_i \times IE_i}$$  \hspace{1cm} (Eq. 1)

Where, $I_i$ is the integrated ion signal (ions or counts) at a $m/z$ over the whole thermal desorption cycle (or over individual heating steps), $X_i$ is the fraction of the signal at $m/z$ from species $i$ and $IE_i$ is the ionization efficiency of species $i$, equaling the number of ions detected per molecule of the parent species. $IE_i$ is species specific and includes not only the EI ionization efficiency but also the transmission efficiency from the oven to the detector, $m/z$-dependent transmission efficiency of the quadrupole mass spectrometer and the detection efficiency of the electron multiplier.

The total mass concentration $C_i$ ($\mu g \text{ cm}^{-2}$) of a particular species $i$ that produce multiple ions at multiple $m/z$ upon EI ionization is:

$$C_i = \frac{10^6 \times MW_i}{X_i \times IE_i \times A \times N_A} \sum_{z=1}^{m-n} I_{i,m/z}$$ \hspace{1cm} (Eq. 2)
where, $MW_i$ is the molecular weight (g mol$^{-1}$) of species i, $A$ is the filter punch area (cm$^2$), $N_A$ is the Avogadro’s number (molecules mol$^{-1}$), $10^6$ is conversion factor from g to μg, and the summation is over all fragment ions in the partial MS of the species.

The species dependent IE and MW are not known for a complex mixture but it has been shown by Jimenez et al. (2003) that $IE/MW_i$ is distinct for inorganics and oxygenated organics and therefore relative $IE$ ($RIE$) can be used to calculate the mass concentration. AMS uses $IE/MW$ of NO$_3^-$ to calculate the $RIE$s of SO$_4^{2-}$, NH$_4^+$, and organics. The TOA-QMS system uses CO$_2$ as an internal calibration and is used for the $IE/MW$ of CO$_2$. Therefore, the $IE/MW_i$ of any organic and inorganic molecule can be expressed as:

$$\frac{IE_i}{MW_i} = RIE_i \frac{IE_{CO2}}{MW_{CO2}} \quad \text{(Eq. 3)}$$

Therefore, $C_i$ can be re-written to include RIEs

$$C_i = \frac{10^6 MW_{CO2}}{X_i \times RIE_i \times IE_{CO2} \times A \times N_A} \sum_{m}^{m=n} I_i, m/z \quad \text{(Eq. 4)}$$

$IE_{CO2}$ is the slope of the CO$_2$ calibration curve (ions per CO$_2$ molecule) for the TOA-QMS system. $RIE$ for NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ are calculated by first calculating the slope for individual moieties (this is essentially $IE$ of individual moieties and will use data from IC analysis and TD mass spectra) and then calculating the $IE/MW$ ratio to CO$_2$. For organics, similar procedure will be employed but using data from many species that have been tested, thus calculating an average $IE_{org}/MW_{org}$ for hydrocarbons and oxidized organics.
$X_i$, fraction of signal from species i at each m/z need be estimated based on a fragmentation table similar to the AMS fragmentation table described in Allan et al. (2004). Since the temperature reached in the TOA-QMS analyzer is higher than that used in the AMS, there is potential for thermal decomposition products from many more compounds. Furthermore, the sample introduction between the TOA-QMS and AMS are very different. Therefore, a fragmentation table specific to TOA-QMS need be developed.

3.2 Computational Analysis

Filter analysis was done with two custom programs developed in MatLab. The first program, named CompleProgram_FINAL, uses the three dimensional raw data created by Agilent’s software to calculate a baseline at each temperature step, for each ion chromatogram, and to integrate peaks until the sample oven temperature is changed. Integration results are automatically normalized with the calibration standard signal. Peak areas are calculated using the Riemann sum method (Riemann, 1868). Data from blank filters may be automatically subtracted from sample data, if desired. Subtraction results are then checked against the limit of detection (LOD) of three standard deviations from the average for each ion fragment determined by the user, and reported if the signal is higher than the LOD. The program allows users to specify the folder or file data to be read from. A final file containing six columns (1 - m/z; 2 - step 1; 3- step 2; 4-step 3; 5-m/z, 6-sum of steps) is created in Excel format. The remaining signals are then analyzed with the program called INORGANIC_COC.m. This program
deconvolutes the data into $\text{NH}_4^+$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$ and OC, and their concentration is calculated.

### 3.3 Considerations for Algorithm Improvement

In case of a baseline change (i.e., drift), the peak area may not be accurate. For example, a step up in the baseline of the chromatogram will cause an overestimation of the signal, while a step down will cause an underestimation. The algorithm may be improved by implementing a running slope method to more accurately determine peak areas. In other words, the slope of the curve needs to be constantly monitored for changes. If the slope becomes zero (i.e. there are no more ions being counted by the mass spectrometer) the program must recognize the end of the step/elution and remain on standby until the next peak shows. One must be careful in applying such correction because of chromatogram noise. An algorithm that recognizes the difference between noise and signal must also be developed.

Another method to determine the area under the curve is to determine the baseline according to the start and ending point of each step, determine a rectangular perimeter under the curve, and divide the tetragon into two triangles. The area of the peak starting from point zero will then be subtracted by the area found under the baseline. Figure 3-1 illustrates the principles of this method as a sketch. The new baseline is represented in red and the area of the peak is the sum of the green rectangles).
Figure 3-1: Proposed alternative method to determine chromatogram baselines. This includes 1) Determining a rectangular perimeter under the curve, 2) Dividing the tetragon into two triangles, 3) Determining a baseline starting point, 4) Calculating the area of the bottom triangle, 5) Calculating the overestimated total area of the peak, and 6) Subtracting the area of the bottom triangle from the total area of the peak.
Chapter 4: Calibration Procedures

4.1 Generation of Calibration Standards

Calibration standards were collected in a cone shaped collector designed by the DRI’s environmental analysis facility (EAF). The collector is composed of a Teflon coated cone capable of holding twelve cartridges containing quartz-fiber and/or Teflon-membrane filters. Aerosols are introduced into the cone from an opening at the top while the filter packs are loaded at the bottom.

Calibration standards were made from aqueous solutions of organic and inorganic compounds diluted to 500 ml. isopropanol and distilled de-ionized (DDI) water, respectively. Solutions were atomized using a constant output atomizer (TSI Precision Measurement Instruments, St. Paul, MN, Model 3076) equipped with a zero-air generator (Environics, Model 7000) and a filtered air supply (TSI, Model 3074B). Organic standards were dried with activated carbon, while inorganic standards were dried with silica gel before being deposited onto the quartz-fiber filters. Filter loadings were individually controlled and adjusted with mass flowmeters (TSI Precision Measurement Instruments, St. Paul, MN, Model 4043) connected to a vacuum pump. Aerosol particle sizes were measured with Scanning Mobility Particle Sizer Spectrometer (SMPS; TSI Precision Measurement Instruments, St. Paul, MN, Model 3936); and a condensation particle counter (CPC) (TSI Precision Measurement Instruments, St. Paul, MN, Model 3775). Information from the SMPS/CPC was used to calculate an approximate amount of
particles deposited on each quartz-fiber filter and to ensure different filter mass loading.

Figure 11 shows the standard filter sample collection set up.

![Image of experimental setup](image)

Figure 4-1. Experimental setup to collect calibration standard aerosol on filters. Key components include: atomizer, diffusion driers, DMA, CPC, cone shape sampling manifold, filter packs and related flow control, and a DustTrak DRX aerosol monitor.

4.2 Fragmentation of Species

In order to obtain the IE of each ion and its respective RIE, the fragmentation pattern from standard quartz-fiber filters containing NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, CO$_2$ and oxalic acid (H$_2$C$_2$O$_4$) were observed. Oxalic acid was chosen since it is a major primary component from biomass burning (Yang et al., 2009) and generally the most abundant and important atmospheric aerosol (Kerminen et al., 2000). Since oxalic acid is used to represent organic compounds, calibrations and calculations utilizing oxalic acid will be
mentioned as organics thereafter. An average of several organic compounds is necessary for a more representative ionization efficiency and calibration procedure.

Inorganic samples were analyzed for fragments of NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$. The observed EI fragmentation was used to determine the species partial mass spectrum, their dependencies on other ions, and to calculate the mass concentration of each species. Total inorganic signals were added and plotted against data obtained from IC analysis with a Dionex ICS – 3000 (Dionex Corporation, Sunnyvale, CA).

By referring back to Equations 1-4, the slope of the linear regression between the TOA-QMS and the IC signal is the IE for each ion. One should take into consideration that random errors may arise when atomizing particles into the quartz-fiber filters and assume that an even coating was applied throughout the filter’s surface. Figure 4-2 to 4-5 show the calibration curves for NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, and OC; the IE of CO$_2$ is shown in Figure 4-6.

The IE of CO$_2$ gas that allowed for the calculation of the RIE was generated by injecting 0.01, 0.025, 0.25, 0.5, 0.75, and 1 mL of 5% CO$_2$/He mixture into the system with a Hamilton GASTIGHT® syringe. Measurements were replicated three times and the average normalized intensity values were used for calculations. Uncertainty in the IE of CO$_2$ was calculated to be ± 0.0021 relative intensity units. Calculation of the mass concentration of CO$_2$ follows Equation 5.
Concentration in $\mu g m^{-3} = \left(\frac{pM_i}{RT}\right) \cdot w \cdot I$  

(Eq. 5)

where $p$ is the pressure of the atmosphere in Pascal, $M_i$ is the molecular weight of the species, $R$ is the gas constant, $T$ is the temperature in Kelvin, $w$ is the mixing ratio of CO$_2$ in ppm, $I$ is the amount of gas that was injected in m$^3$.

Figure 4-2. Calibration curve for ammonium ion. Error bars of 1 standard deviation are shown.
Figure 4-3. Calibration curve for nitrate ion. Error bars of 1 standard deviation are added to the graph although very small to provide visual insight.

Figure 4-4. Calibration curve for sulfate ion. Error bars of 1 standard deviation are shown.
Figure 4-5. Calibration curve for organic species (i.e., organic carbon). Error bars of 1 standard deviation are shown.

Figure 4-6. Ionization efficiency curve for CO₂. Error bars of 1 standard deviation are added to the graph although very small to provide visual insight.
Fragments of NH$_4^+$, observed by El-QMS analysis of (NH$_4$)$_2$SO$_4$, were accounted into the IE curve at m/z 15 (NH$^+$), m/z 16 (NH$_2^+$), and m/z 17 (NH$_3^+$). Signals at m/z 16 were considered to be completely from the dissociation of NH$_4^+$. The signal at m/z 17 related to NH$_4^+$ fragmentation was calculated by removing the fraction that represents the fragments from H$_2$O (i.e., OH$^+$). Observation of the signal intensities at m/z 18 and m/z 17 from the NIST database shows that 21% of the signal at m/z 18 fragments into m/z 17. Therefore, 21% of the signal from m/z 18 is subtracted from the signal at m/z 17.

Fragments of NO$_3^-$ were accounted for into the IE curve at m/z 30 (NO$^+$) and m/z 46 (NO$_2^+$). According to the fragmentation pattern, these two signal account for 72.75 ± 12.62% of the total nitrate signal. Therefore, like the AMS, it was observed that a correction factor (cf) that includes the omitted fragments is necessary (Hogrefe et al., 2004) to correctly estimate the mass concentration of inorganic NO$_3^-$ aerosol on quartz-fiber filters.

Fragments of sulfate were accounted for into the IE curve from m/z 18 to m/z 102. The major species (m/z 18[H$_2$O$^+$], m/z 48 [SO$^+$], and m/z 64 [SO$_2^+$]) account for 77.28 ± 14.48% of the total signal. In order to best estimate the sulfate contribution fraction at m/z 18, the signal was correlated to m/z 48 and m/z 64. As a result, m/z 18 was found to be 0.49 * signal at m/z 48 + 0.268 * signal at m/z 64.

In the case of the N$^+$ ion fragment (m/z 14), observed from the analysis and dissociation of NH$_4$NO$_3$, an experimental fraction value was found in order to distinguish
between its origins from NH$_4^+$ or NO$_3^−$. Because the dissociation of NH$_4^+$ does not yield $m/z$ 30 (NO$^+$) or $m/z$ 46 (NO$_2^+$), the fraction of $m/z$ 14 as a product from the dissociation of NO$_3^+$ was found by observing the ratio between $m/z$ 14 (N$^+$) and $m/z$ 30 (NO$^+$) and the ratio between $m/z$ 14 and $m/z$ 46 (NO$_2^+$). The ratios observed represent the fraction of $m/z$ 14 generated from the dissociation of NO$^+$ and NO$_2^+$. The remainder of the signal was attributed to the dissociation of NH$_4^+$.

Organic fractions were estimated after accounting for the inorganic species. In the case that organic fragments correspond to the same $m/z$ as inorganics, the previously described process of finding relationships between species was used. The same process is used to establish the AMS fragmentation table. A more detailed explanation on this process can be found on the field data analysis guide from Jimenez’s research group (Jimenez, 2014) and by Allan et al. (2004).

The developed fragmentation tables for NO$_3^−$, SO$_4^{2−}$, and NH$_4^+$, along with organics that are used to estimate mass concentration follow the same format as described by Allan et. al (2004). Fragment contributions marked with a superscript “a” use factors based on predicted contributions from known isotopes predicted based on the International Union of Pure and Applied Chemistry (IUPAC) recommended isotopic abundances. Those marked with a superscript “b” are based on laboratory analysis. Numbers in brackets represent the total observed signal for the ion with specified $m/z$, commas denote addition, * denotes multiplication, and – denotes subtractions.
Table 4-1. Fragmentation pattern observed for nitrate. Fragment contributions marked with a superscript “a” use factors based on predicted contributions from known isotopes. Those marked with a superscript “b” are based on laboratory analysis.

<table>
<thead>
<tr>
<th>m/z</th>
<th>frag_Nitrate</th>
<th>frag_Organic</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>0.0178*frag_nitrate[30]b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.17818*frag_nitrate[46]b</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>[30], - frag_organic[29]</td>
<td>0.022*[29]a</td>
</tr>
<tr>
<td>31</td>
<td>0.00405*frag_nitrate[30]a</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>0.002*frag_nitrate[30]a</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>[46]</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>0.00443*frag_nitrate[46]a</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>0.004*frag_nitrate[46]a</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-2. Fragmentation table observed for sulfate. Fragment contributions marked with a superscript “a” use factors based on predicted contributions from known isotopes. Those marked with a superscript “b” are based on laboratory analysis.

<table>
<thead>
<tr>
<th>m/z</th>
<th>frag_Sulfate</th>
<th>frag_Organic</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>[48], - frag_nitrate[48]</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>[64], - frag_organic[64]</td>
<td>0.5*frag_organic[50]b,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5*frag_organic[78]b</td>
</tr>
</tbody>
</table>

Table 4-3. Fragmentation table observed for ammonium. Fragment contributions marked with a superscript “a” use factors based on predicted contributions from known isotopes. Those marked with a superscript “b” are based on laboratory analysis.

<table>
<thead>
<tr>
<th>m/z</th>
<th>frag_NH4</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>[14], - frag_nitrate[14]</td>
</tr>
<tr>
<td>15</td>
<td>0.0802*[16]b</td>
</tr>
<tr>
<td>16</td>
<td>[16]</td>
</tr>
<tr>
<td>17</td>
<td>[17], -0.2122*frag_water[18]a</td>
</tr>
</tbody>
</table>

4.3 Reproducibility

The reproducibility of the TOA-QMS was briefly tested by observing the change in RIEs of the inorganic and organic molecules that were collected as standards. Calculation of RIEs is relevant in comparing data between periods of time, allowing for good agreement and comparison between IC and TOA-QMS mass concentration calculations. Assuming that the composition and mass loadings of the filters were maintained during freezer storage, analysis of standards were done in June 2014, December 2015, and March 2015 and the RIEs calculated for each species. December 2014 tests were done after a change in the capillary transfer line. Tests in March 2015 were done while maintaining the same instruments conditions as in December 2014. Figure 4-7 and Table 4-4 show the calculated RIE of \( \text{NH}_4^+ \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \) and organics relative to \( \text{CO}_2 \) over the experimental time periods.

For the periods between June 2014 through December 2014, \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) are relatively constant, \( \text{SO}_4^{2-} \) suffers a slight increase, and organics continuously decrease. From December 2014 to March 2015 \( \text{NH}_4^+ \) and \( \text{NO}_3^- \) and organic RIE continues to decrease, while \( \text{SO}_4^{2-} \) RIE increases.

It is speculated that changes in RIE are most likely caused by oxidation of the MS ion repeller and filament and degradation of the transfer capillary line, causing a decrease in instrument sensitivity. The oxidation of the MS filament in the presence of \( \text{O}_2 \) has been demonstrated by Mauersberger et al. (1973).
RIE values are attained with rearrangement of Equation 3 (as Equation 6). That is, the ratio of the slope obtained from each ionic species to the slope obtained from CO$_2$ analysis makes it possible to calculate the RIE of the system for each aerosol component.

\[
RIE_i = \frac{IE_i}{MW_i} \times \frac{MW_{CO_2}}{IE_{CO_2}} \tag{Eq. 6}
\]

According to these results, it is clear that maintenance of the system and a change and/or improvements to the fragmentation table requires new calibration curves and RIEs to be calculated. Testing of the long term stability of the system needs to be investigated.
Table 4-4. Relative ionization efficiencies of inorganic and organic species monitored from June 2014 to March 2015.

<table>
<thead>
<tr>
<th>Aerosol Component</th>
<th>RIE (Relative to CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Jun-14</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.33</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.23</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>6.06E-02</td>
</tr>
<tr>
<td>Organics</td>
<td>1.47</td>
</tr>
</tbody>
</table>
Chapter 5: Application to Ambient Samples

5.1 Mass Spectra for Calibration Standards

To evaluate the performance of the TOA-MS, the TOA-MS spectra for non-light absorbing calibration compounds were compared to those from the AMS and the National Institute of Standards and Technology (NIST) EI database (Hogrefe et al., 2004; Stephen, 2011).

The mass spectra of NH$_4$NO$_3$ from TOA-MS and QMS are compared in Figure 5-1. It is observed that the TOA-QMS shows ion peaks at the same m/z as those by the AMS, with peaks observed at m/z 14 (N$^+$), 15 (NH$^+$), 16 (NH$_2^+$), 17 (NH$_3^+$), 18 (NH$_4^+$), 30 (NO$^-$), and 46 (NO$_2^+$). However, the relative intensities of these peaks between these two instruments are different. TOA-QMS also shows an interference CO$_2$ signal at m/z 44.

The difference in spectra of the same compound between the TOA-QMS and the AMS are possibly caused by differences in heating rate, particle collection medium, thermal desorption and ionization environment.

The mass spectrum of (NH$_4$)$_2$SO$_4$ in Figure 5-2 shows ion peaks at m/z 14 (N$^+$), 15 (NH$^+$), 16 (NH$_2^+$), 17 (NH$_3^+$), 18 (NH$_4^+$), 32 (S$^+$), 48 (SO$^+$), and 64 (SO$_2^+$) for both TOA-QMS and AMS. However, it is not known why peaks at m/z 80 (SO$_3^+$), 81 (SO$_3^+$, HSO$_3^+$) and 98 (H$_2$SO$_4^+$) were not detected by the TOA-QMS.
Figure 5-1. Spectra of NH$_4$NO$_3$ by TOA-QMS and Q-AMS. The most abundant peaks of NH$_4$NO$_3$ are observed at m/z 14, 15, 16, 17, 18, 30, and 46.

Figure 5-2. Spectra of (NH$_4$)$_2$SO$_4$ by TOA-QMS and Q-AMS. The most abundant peaks for (NH$_4$)$_2$SO$_4$ are observed at m/z 14, 15, 16, 17, 18, 32, 48, 64, 80, 81, and 98.

5.2 Ambient PM$_{2.5}$ Samples

To validate the TOA-QMS measurement, ambient PM$_{2.5}$ samples were analyzed by the TOA-QMS, IC, and TOA carbon analyzer. A total of 100 filters, including replicates
were re-analyzed. The selected samples include 58 samples with 16 replicates from the Fresno Supersite collected during the wintertime of 2000-2001, 11 samples from Baltimore, MD, and three samples from the Fresno Supersite, CA collected in winter, spring, and summer (5 replicates each). Previous IC analysis has shown high sulfur content with Baltimore samples, and high NO$_3^-$ content with Fresno samples.

Before TOA-QMS analysis, particle laden quartz-fiber filters were analyzed with IC for ions and DRI’s Model 2001 carbon analyzer for OC and EC, amongst other methods (Watson et al., 2002a). Figure 5-3 to Figure 5-6 compare mass concentration of the ions and OC measured by TOA-QMS with those by IC and TOA. The instruments comparison indicate the uniqueness and capability of the TOA-QMS technique and its capability to quantify and identify organic and inorganic aerosols species from archived filter samples.

Compared to IC analysis, TOA-QMS ambient sample measurements showed an average understatimation of 24% for NO$_3^-$ and an overestimation of 29% for SO$_4^{2-}$ when forcing the linear regression through the origin. These uncertainties are similar to those reported by the AMS for inorganic measurements of 26% when calibrated with PILS (Canagaratna et al., 2007). The larger disagreement of ambient samples mass concentrations between IC and TOA-QMS for NO$_3^-$ (Figure 5-4) and SO$_4^{2-}$ (Figure 5-5) are likely due to interference between organic and inorganic signals, or the formation of different species as fragmentation occurs. It is known that IC SO$_4^{2-}$ does not include insoluble organosulfate (e.g., COSO$_3$) and some insoluble sulfate salts (e.g. BaSO$_4$,
PbSO$_4$, Ag$_2$SO$_4$ and SrSO$_4$) (Hawkins et al., 2010). Therefore, the IC might underestimate total SO$_4^{2-}$. The implementation of a correction factor for SO$_4^{2-}$ and NO$_3^-$ ions in order to better fit the curve is discussed in the next section.

Figure 5-3. TOA-QMS mass concentration of NH$_4^+$ plotted vs. IC mass concentration of NH$_4^+$. Error bars of ± 1 standard deviation are shown. Only samples with values above the detection limit are plotted.

Figure 5-4. TOA-QMS mass concentration of NO$_3^-$ plotted vs. IC mass concentration of NO$_3^-$. Error bars of ± 1 standard deviation are shown. Only samples with values above the detection limit are plotted.

Figure 5-5. TOA-QMS mass concentration of SO$_4^{2-}$ plotted vs. IC mass concentration of SO$_4^{2-}$. Error bars of ± 1 standard deviation are shown although very small. Only samples with values above the detection limit are plotted.

Figure 5-6. TOA-QMS mass concentration of organics plotted vs. OC mass concentration by DRI Model 2001 TOA. Error bars of ± 1 standard deviation are shown. Only samples with values above the detection limit are plotted.
For the wintertime Fresno Supersite study only (58 samples), quartz-fiber filters were used to collect PM$_{2.5}$. Particle collection was done with a medium-volume sequential filter samplers at 20 L/min for each channel with Bendix 240 cyclones. The average fraction of particulate NH$_4^+$, SO$_4^{2-}$, NO$_3^-$, and OC for the 2000-2001 Fresno Supersite winter samples are presented as bar charts in Figure 5-7. Note that contribution from metals, salts, and EC are not included into the chart. A very small percent difference was observed between the different types of analysis used for comparison. As measurements are chemical composition dependent, average percent differences observed between the TOA-QMS and IC or TOA were observed to be 2% for NH$_4^+$, 1% for SO$_4^{2-}$, 2% for NO$_3^-$, and 3% for organic species. Such small differences indicates that measures by the TOA-QMS and IC/TOA are highly comparable when several filters are used for data collection.

![TOA-QMS vs IC and TOA](image)

Figure 5-7. Average concentration partition of organic and inorganic species for the 58 filters collected from the Fresno Supersite measured by TOA-QMS and by IC and TOA.
The time series of \( \text{NH}_4^+ \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), and organics for the wintertime Fresno Supersite study during 12/15/2000 – 2/3/2001 are shown in Figure 5-11. \( \text{NH}_4^+ \), \( \text{NO}_3^- \), and organics closely track each other. While TOA-QMS is also able to track \( \text{SO}_4^{2-} \) temporal changes, it overestimated mass concentration values from 12/27/2000 to 01/07/2001, consistent with Figure 5-5. Nonetheless, data analysis proves the TOA-QMS reliability in studying pattern changes of different species over a long period.

Figure 5-12 shows a stack bar graph of \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), and OC concentrations from the Fresno samples during 12/15/2000 – 2/3/2001 and provides better insight on the relationship between each species over time. The concentrations of all species were observed to rise on 12/27/2000 until 1/7/2001 due to a long period of haze observed over Fresno. Unfortunately, quartz-fiber filters for most of the month of January 2001 was not available for TOA-QMS analysis. However, lower levels of inorganic and organic aerosol fractions can be seen in middle of December 2000 and the beginning of February 2001. \( \text{PM}_{2.5} \) \( \text{NO}_3^- \) concentrations for the beginning of January are almost as high as OC concentration, indicating that \( \text{NO}_3^- \) may contribute significantly to episodes of poor air quality. An increase in the level of \( \text{NH}_4^+ \) is also observed during high levels of \( \text{NO}_3^- \) and organic particulates. The increase in concentrations are most likely also related to residential wood combustion and vehicle emissions that can be trapped in an inversion layer during the colder days along with the lower temperature favoring \( \text{NO}_3^- \) to be in particle phase (Chow et al., 2008b; Grover et al., 2006; Watson et al., 2000; Watson et al., 2002b).
Figure 5-8. Time series comparison between TOA-QMS and IC of particulate NH$_4^+$ mass concentrations.

Figure 5-9. Time series comparison between TOA-QMS and IC of particulate NO$_3^-$ mass concentrations.

Figure 5-10. Time series comparison between TOA-QMS and IC of particulate SO$_4^{2-}$ mass concentrations.

Figure 5-11. Time series comparison between TOA-QMS and TOA organic carbon analysis mass concentrations.
Figure 5-12. Daily concentration for measured organic and inorganic species using the TOA-QMS method for the Fresno Supersite study from December 15, 2000 to February 3rd, 2001.

5.3 Correction Factors

Applying a correction factor (CF) is a common practice when comparing AMS with other instruments (Drewnick et al., 2003; Hogrefe et al., 2004; Jimenez et al., 2003) to account for ions not included in the calibration curve. Correction factors were not applied to the mass concentrations to the data above. Further development of the fragmentation table is needed in order to improve mass concentration measurements.

CFs for NO$_3^-$ and SO$_4^{2-}$ are calculated by dividing the TOA-QMS concentration by the IC concentration. The averages CFs are 1.36 and 0.80 for NO$_3^-$ and SO$_4^{2-}$, respectively. Applying the NO$_3^-$ CF increased the regression slope between TOA-QMS and IC from 0.72
in Figure 5-4 to 0.98 in Figure 5-13. Similarly, application of the NO$_3^-$ CF improved the slope from 1.19 in Figure 5-5 to 1.00 in Figure 5-14.

Correction factors for NH$_4^+$ and OC could not be justified at the moment. This is the case since all of the signal for NH$_4^+$ and oxalic acid were accounted for when calculating the values for the calibration table. In addition, unlike SO$_4^{2-}$, NH$_4^+$ is very well defined by IC. Lastly, comparison between sample values obtained with TOA-QMS vs IC and TOA show slopes of 0.94 for NH$_4^+$ and 0.99 for OC.

![Ambient Nitrate Ion (Cf)](image)

Figure 5-13. TOA-QMS mass concentration of nitrate ion adjusted with a correction factor of 1.36 plotted vs. IC mass concentration.
Figure 5.14. TOA-QMS mass concentration of sulfate ion adjusted with correction factors of 0.80.

5.2 Detection Limit, Precision, and Accuracy

The minimum method detection limit (MDL) for each specie was calculated by applying the fragmentation table to blank quartz-fiber filter punches or, in case no signal was detected by the El-QMS, the linear regression was used (Regulations, 2000). The MDL of $\text{NH}_4^+$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$, and organic species were 1.59 ug cm$^{-2}$, 0.07 ug cm$^{-2}$, 0.96 ug cm$^{-2}$, and 4.22 ug cm$^{-2}$, respectively. Method detection limit (MDL) for OC with DRI Model 2001 TOA is 0.43 ug cm$^{-2}$, and inorganic species with IC are 0.10 ug cm$^{-2}$. The calculated average precision and standard deviation in measurements for uncorrected samples are, 0.03 ± 0.80 ug cm$^{-2}$ for $\text{NH}_4^+$, 0.02 ± 1.94 ug cm$^{-2}$ for $\text{NO}_3^-$, 0.03 ± 0.41 ug cm$^{-2}$ for $\text{SO}_4^{2-}$, and ± 0.046 ± 1.26 ug cm$^{-2}$ for organic species. More investigation is necessary in order to determine the MDL since different laboratory blank filter sets currently provide different MDL values. Calculation of the LOD before daily sample analysis could be proven more useful.
Chapter 6: Elemental Analysis of Organic Species

6.1 Introduction

As it has been shown in Chapter 5, quantification of NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, and OC is possible with the TOA-QMS. However, more information may be extracted from ambient samples with this technique. In particular, further analysis of the mass spectrum may provide more qualitative information. That is, deconvolution of the mass spectra can provide information of the organic aerosol composition and aid with source apportionment models. Elemental analysis (EA) of organic mixtures (C, H, N, S, and O) is of current interest because the oxygen-to-carbon (O/C), hydrogen-to-carbon (H/C), nitrogen-to-carbon (N/C), and sulfur-to-carbon (S/C) elemental ratios can be used to calculate the total organic mass (OM) to organic carbon (OC) ratio.

Since usually only OC is directly measured and organic H, N, S, and O are not quantified, OM is estimated by multiplying OC by a organic-mass-to-organic-carbon (OM/OC) ratio (Chow et al., 2015a; Pang et al., 2006). A factor of 1.4 - 1.8 is traditionally used (Chow et al., 2015a and references therein). Depending on the oxidation state of OM, factors range from 1.2 for fresh aerosol in urban areas (Chow et al., 2002a; 2002b) to 2.6 for aged aerosols (Countess et al., 1980; Robinson et al., 2007; Robinson et al., 2010; Roy et al., 2011; Turpin and Lim, 2001). Commercially available elemental analyzers (EA) can analyze C, H, N, S, and O. However, typically relatively large sample quantities (~1 mg) are needed due to their low sensitivity. Therefore, these analyzers are not
suitable for analyzing ambient PM samples. The development of a new technique that requires much smaller sample size while providing fast analysis is of great interest for environmental applications.

Current available techniques for measurement of small samples include nanoaerosol mass spectrometry (NAMS), the Electron Impaction Ionization-High Resolution-Aerosol Mass Spectrometer (EI-HR-AMS), and the unit-mas resolution (UMR) AMS. The NAMS performs EA on individual particles of less than 10 nm in diameter by collecting particles in an ion trap and decomposing them into atomic ions by high-energy laser ablation (Wang et al., 2006), while the HR-AMS and the UMR AMS rely on assuming the elemental composition of the ions (Aiken et al., 2007). Advantage of the UMR-MS technique for EA is a fast, cost-effective, and sensitive approach to approximate the aerosol elemental composition when compared to the HR-AMS. The potential of this technique has been explored with the TOA-QMS for EA of particle-laden quartz-fiber filters.

The EA technique relies on the assumption that the sum of the ion signal intensities from all fragments, especially for molecules containing small atoms, is approximately proportional to the mass concentration of the original species. As a result, the same ion current at different m/z’s represents the same original mass and allows for the average composition of the ions to be calculated. For example Aiken et al. (2007) points out that if there is a 1 kHz signal at m/z 60 and 300 for one of two species, the same approximate mass of both species were present in the ionization region. Therefore, 5 times more
fragments of the lighter molecule must have been present. The estimate of the molecular or mixture composition can then be found by adding the relative ions contributions in the mass spectrum after separating the composition of the signal between the estimated atoms present at each fragment. Measured atomic ratios by mass spectra are then converted to estimated ratios by using a correction factor determined from the analysis of known organic standards (Aiken et al., 2007).

The validation of the EA technique was initially tested with 21 mass spectra with molecular mass (MM) ranging from 16 g/mol to 90 g/mol (Aiken et al., 2007). Elemental analysis of these molecules demonstrated a high correlation between the nominal and the EA calculated ratios, showing that the chemical bias during molecular fragmentation are not large enough to suppress the O/C and H/C information for small molecules. It was argued that the use of small molecules to test EA using UMR EI mass spectra was necessary in order to unambiguously determine the ion signal composition. However, it is shown that good estimations can achieved with large molecules

Although the TOA-QMS operates at UMR and prior separation is not applied to samples, observed mass spectra suffers from the fact that different ion fragment may coexist at the same ion signal. A recent advancement in EA using UMR that may aid in future analysis with the TOA-QMS relies on the use of isotopic labeling (Hicks et al., 2015). Nonetheless, a preliminary effort was made to apply EA to organic samples analyzed with the TOA-QMS.
6.2 Organic Standard Sample Analysis

Twenty one organic compounds with known compositions were first measured by TOA-QMS to assess its performance for elemental analysis. These organic compounds represent O/C, H/C, and OM/OC ratios of primary, secondary, and ambient organic aerosols (Aiken et al. 2007; 2008). Table 6-1 shows the analyzed organic compounds.

In order to test the EA method, and establish the analysis procedure, oxalic acid was first analyzed using the NIST mass spectrum (Table 6-2). The same signal abundances and ratios are observed as those by Aiken et al. (Aiken et al., 2007). The EA average elemental composition in this case is the weighted average of the composition between the two observed ions. Therefore, the best approximation of the fractions of a complex mixture will yield the best average elemental composition. The best composition can be found by summing each ion contribution in the mass spectrum. As Aiken et al. (2007) points out, for an organic spectrum, the relative mass concentrations of C and O can be estimated as:

\[ M_c = \sum_{j=m/z_{min}}^{j=m/z_{max}} I_j F_c \]  
\[ M_o = \sum_{j=m/z_{min}}^{j=m/z_{max}} I_j F_o \]  
(Eq. 8)  
(Eq. 9)

where \( I_j \) is the ion m/z at the \( j^{th} \) peak in the spectrum and \( F_c \) and \( F_o \) are the mass fractions of C and O in each ion (e.g., \( F_c = 12/46 \) and \( F_o = 12/46 \) for \( CH_2O_2^+ \)). The O/C and H/C mass ratios can then be calculated as \( M_o/M_c \) (Aiken, et al., 2007).
Table 6-1. Organic compounds analyzed with the TOA-QMS with the EA technique.

<table>
<thead>
<tr>
<th>no.</th>
<th>Class</th>
<th>Subclass</th>
<th>Compound</th>
<th>MM (g/mol)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>hydrocarbon</td>
<td>alkane</td>
<td>methane</td>
<td>16.04</td>
<td>CH₄</td>
</tr>
<tr>
<td>2</td>
<td>alcohol</td>
<td>alkanol</td>
<td>1-octadecanol</td>
<td>270.49</td>
<td>C₁₈H₃₈O</td>
</tr>
<tr>
<td>3</td>
<td>alkanol</td>
<td>alkanol</td>
<td>1-eicosanol</td>
<td>298.55</td>
<td>C₂₀H₄₀O</td>
</tr>
<tr>
<td>4</td>
<td>alkanol</td>
<td>alkanol</td>
<td>1-docosanol</td>
<td>326.6</td>
<td>C₂₂H₄₄O</td>
</tr>
<tr>
<td>5</td>
<td>dialkanol</td>
<td>1,2-tetradecanediol</td>
<td></td>
<td>230.39</td>
<td>C₁₄H₂₂O₂</td>
</tr>
<tr>
<td>6</td>
<td>phenol</td>
<td>pyrogallol</td>
<td></td>
<td>126.11</td>
<td>C₆H₈O</td>
</tr>
<tr>
<td>7</td>
<td>sterol</td>
<td>cholesterol</td>
<td></td>
<td>386.65</td>
<td>C₂₅H₄₆O</td>
</tr>
<tr>
<td>8</td>
<td>carboxylic acid</td>
<td>alkanoic acid</td>
<td>decanoic acid</td>
<td>172.27</td>
<td>C₁₀H₂₀O₂</td>
</tr>
<tr>
<td>9</td>
<td>alkanoic acid</td>
<td>alkanoic acid</td>
<td>pentadecanoic acid</td>
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<td>alkanoic acid</td>
<td>hexadecanoic acid</td>
<td>256.42</td>
<td>C₁₆H₃₂O₂</td>
</tr>
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<td>11</td>
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<td>alkanoic acid</td>
<td>stearic acid</td>
<td>284.48</td>
<td>C₁₈H₃₆O₂</td>
</tr>
<tr>
<td>12</td>
<td>alkanoic acid</td>
<td>alkanoic acid</td>
<td>oleic acid</td>
<td>282.46</td>
<td>C₁₈H₃₀O₂</td>
</tr>
<tr>
<td>13</td>
<td>dicarboxylic acid</td>
<td>dicarboxylic acid</td>
<td>glutaric acid</td>
<td>132.12</td>
<td>C₆H₁₀O</td>
</tr>
<tr>
<td>14</td>
<td>dicarboxylic acid</td>
<td>dicarboxylic acid</td>
<td>adipic acid</td>
<td>146.14</td>
<td>C₆H₁₀O₄</td>
</tr>
<tr>
<td>15</td>
<td>hydro-carboxylic acid</td>
<td>hydro-carboxylic acid</td>
<td>15-hydroxypentadecanoic acid</td>
<td>258.42</td>
<td>C₁₅H₃₀O₃</td>
</tr>
<tr>
<td>16</td>
<td>hydro-carboxylic acid</td>
<td>hydro-carboxylic acid</td>
<td>16-hydroxyhexadecanoic acid</td>
<td>272.43</td>
<td>C₁₆H₃₂O₃</td>
</tr>
<tr>
<td>17</td>
<td>carbohydrate</td>
<td>monosaccharide anhydride</td>
<td>levoglucosan</td>
<td>162.14</td>
<td>C₆H₁₀O₄</td>
</tr>
<tr>
<td>18</td>
<td>amine</td>
<td>amino acid</td>
<td>4-aminobenzoic acid</td>
<td>137.14</td>
<td>C₇H₇NO₂</td>
</tr>
<tr>
<td>19</td>
<td>alkaloid</td>
<td>quinine</td>
<td></td>
<td>324.42</td>
<td>C₂₀H₂₁N₃O₂</td>
</tr>
<tr>
<td>20</td>
<td>organic nitrite</td>
<td>phenyl nitrite</td>
<td>3-methyl-4-nitrophenol</td>
<td>153.14</td>
<td>C₇H₇NO₃</td>
</tr>
<tr>
<td>21</td>
<td>anhydride</td>
<td>Carbon Dioxide</td>
<td></td>
<td>44.01</td>
<td>CO₂</td>
</tr>
</tbody>
</table>
Table 6-2 Oxalic Acid El Spectrum from the NIST database as processed by EA technique primarily developed for HR-AMS (Aiken et al., 2007). The mass fraction of individual atoms at each fragment is apportioned to the signal abundance found at the corresponding m/z. Each signal corresponding to the specific atom is summed and the atomic ratio calculated using the mass ratios of each atoms (e.g., \([\text{total O signal/16}]/[\text{total C signal/12}]\).

<table>
<thead>
<tr>
<th>m/z</th>
<th>Fragment ID</th>
<th>ABUNDANCE (%)</th>
<th># of C</th>
<th># of H</th>
<th># of O</th>
<th>C Signal</th>
<th>H Signal</th>
<th>O Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>C</td>
<td>20</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>20.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>16</td>
<td>O</td>
<td>30</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
<td>30.00</td>
</tr>
<tr>
<td>17</td>
<td>OH</td>
<td>100</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0.00</td>
<td>5.88</td>
<td>94.12</td>
</tr>
<tr>
<td>18</td>
<td>H₂O</td>
<td>210</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>0.00</td>
<td>23.33</td>
<td>186.67</td>
</tr>
<tr>
<td>28</td>
<td>CO</td>
<td>610</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>281.43</td>
<td>0.00</td>
<td>348.57</td>
</tr>
<tr>
<td>29</td>
<td>CHO</td>
<td>320</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>132.41</td>
<td>11.03</td>
<td>176.55</td>
</tr>
<tr>
<td>44</td>
<td>CO₂</td>
<td>280</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>76.36</td>
<td>0.00</td>
<td>203.64</td>
</tr>
<tr>
<td>45</td>
<td>CHO₂</td>
<td>999</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>266.40</td>
<td>22.20</td>
<td>710.40</td>
</tr>
<tr>
<td>46</td>
<td>CH₂O₄</td>
<td>800</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>208.70</td>
<td>34.78</td>
<td>556.52</td>
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<tr>
<td>47</td>
<td>CH₂O₃</td>
<td>20</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>5.11</td>
<td>0.85</td>
<td>13.62</td>
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<tr>
<td>56</td>
<td>C₂O₂</td>
<td>50</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>21.43</td>
<td>0.00</td>
<td>28.57</td>
</tr>
<tr>
<td>72</td>
<td>C₃O₃</td>
<td>10</td>
<td>2</td>
<td>0</td>
<td>3</td>
<td>3.33</td>
<td>0.00</td>
<td>6.67</td>
</tr>
<tr>
<td>90</td>
<td>C₅H₇O₄</td>
<td>20</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>5.33</td>
<td>0.40</td>
<td>14.22</td>
</tr>
</tbody>
</table>

Next, organic standard compounds ranging from 16 g/mol to 386 g/mol were atomized and collected onto quartz-fiber filters with the setup described in Chapter 4 and shown in Figure 4-1. Each organic compound was collected on six different filters with varying mass loading. Some of these filters were excluded in creating an averaged point for the calibration curve due to contamination of siloxane identified by the combination of peaks at m/z 205, 207, 281, and 355, or because of too low mass loading. Figure 6-1 to 6-4 shows the measured elemental ratios for O/C, H/C, and N/C, and the OM/OC by the TOA-QMS vs. the nominal ratios of the pure compounds. The
results demonstrate that the bias during fragmentation is low and the resulting spectra are similar to the one found with EA of the NIST data.

The O/C ratio (Figure 6-1) by TOA-QMS shows excellent agreement with the nominal values (slope = 0.936 and $R^2 = 0.97$) However, the TOA-QMS systematically underestimates O/C slightly. This has been observed in the (Aiken et al., 2007), and is attributed to the fact that fragments with low O$_2$ content have a weaker tendency to retain a positive charge during fragmentation, as expected based on its electronegativity (McLafferty and Turecek, 1993). On the other hand, the slope of the regression line (0.93 ± 0.036) indicates that the electronegativity effect of the O$_2$ does not cause a significant underestimation. The average error in the estimated O/C after applying the correction factor is 29% compared to 31% for the same analysis with the HR-AMS (Aiken et al., 2008).

Figure 6-2 shows that the H/C ratios have a larger underestimation (slope 0.77) than the O/C ratios. Such underestimation is likely due to losses of H and H$_2$ during fragmentation and the absence of m/z below 10 (Aiken et al., 2007). The measured and nominal H/C correlates reasonably well ($R^2 = 0.83$) and is similar with the $R^2$ of 0.92 found with EA of the NIST data by HR-AMS (Aiken et al., 2007; Aiken et al., 2008). The average error in the estimated H/C after applying the correction factor is 9.2 % compared to 10% for the same analysis with the HR-AMS (Aiken et al., 2008).
Figure 6-1. O/C determined with TD-MS laboratory standards vs. the nominal O/C of the pure compounds. Error bars of 1 standard deviation and linear regression though the origin is presented.

Figure 6-2. H/C determined with TOA-QMS laboratory standards vs. the nominal H/C of the pure compounds. Error bars of 1 standard deviation and linear regression though the origin is presented.
Figure 6-3 shows preliminary analysis of the N/C ratio. Although the good correlation ($R^2 = 0.99$) indicates that the method is promising for N/C quantification, additional calibration points are needed to calculate a correction factor that is more representative or nitrogen containing organic compounds before it can be fully integrated into the TOA-QMS EA technique. Organic nitrogen typically represents a smaller fraction of the organic aerosol. The N/C regression slope is $0.75 \pm 0.06$, and the average error is estimated to be 5.6% compared to 22% for the same analysis with the HR-AMS (Aiken et al., 2008). S/C was not explored because of the lack of sulfur containing atomized standard compounds.

Figure 6-3. N/C determined with TOA-QMS laboratory standards vs. the nominal N/C of the pure compounds. Error bars of 1 standard deviation and linear regression though the origin is presented.
The observed correlation between the estimated and nominal ratios of O/C, H/C, and N/C indicate that, after calibration, the EA by the TOA-QMS is able to reasonably estimate the elemental ratios of organic compounds.

6.3 OM/OC Estimation

Estimation of the OM/OC was calculated based on values found for O/C, H/C, and N/C according to Equation 7 (Aiken et al., 2007). Figure 6-4 shows the measured and nominal OM/OC ratios of all organic standard compounds listed in Table 6-1. The slope of the line is 0.94 ± 0.043 and the intercept is 0.034, with an average error of 4.0% for individual compounds.

\[
\frac{OM}{OC} = \left(16 \times \frac{O}{C}\right) + \left(1 \times \frac{H}{C}\right) + \left(14 \times \frac{N}{C}\right) + 12
\]  
(Eq. 7)

The complete data from EA of all standard organic compounds is presented in Table 6-3. These compounds are grouped by organic classification, molecular formulas, molecular mass (MM), and nominal and measured raw atomic ratios (O/C, H/C, N/C and OM/OC). The close agreement of measured and nominal OM/OC indicates that the TOA-QMS is able to determine QM/OC reasonably accurately for single organic species.
Figure 6-4. OM/OC determined from the calibrated atomic ratios of the TOA-QMS organic standards with error bars of 1 standard deviation vs. the OM/OC of the pure compounds.

A graphical comparison between EA using a HR-AMS and the TOA-QMS for the same samples is plotted in Appendix D from Figures D-1 through D-3. Different software packages introduce bias to data analysis. Compared to Microsoft Excel, IGORPRO graphical representation of O/C, H/C, and N/C calibration values are different than values obtained with Microsoft Excel. Figures D4 – D7 show the calibration curve for of O/C, H/C, and N/C prepared with IGORPRO. OM/OC remains the same when using the two software packages.
Table 6-3 List of compounds analyzed by EA with the TOA-QMS grouped by organic classification, molecular formulas, MM (mg/mol), and nominal and calculated raw atomic ratios (O/C, H/C, N/C and OM/OC) with one standard deviation are present

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>MM</th>
<th>Formula</th>
<th>O/C</th>
<th>O/C _ EA calc ± σ</th>
<th>H/C</th>
<th>H/C _ EA calc ± σ</th>
<th>N/C</th>
<th>N/C _ EA calc ± σ</th>
<th>OM/OC</th>
<th>OM/OC _ EA calc ± σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrocarbon</td>
<td>methane</td>
<td>16.04</td>
<td>C\textsubscript{2}H\textsubscript{6}O</td>
<td>0.06</td>
<td>0.05 ± 0.014</td>
<td>2.11</td>
<td>1.67 ± 0.013</td>
<td>1.33</td>
<td>1.25 ± 0.001</td>
<td>1.25</td>
<td>1.20 ± 0.018</td>
</tr>
<tr>
<td>alcohol</td>
<td>1-octadecanol</td>
<td>270.49</td>
<td>C\textsubscript{15}H\textsubscript{32}O</td>
<td>0.05</td>
<td>0.07 ± 0.058</td>
<td>2.10</td>
<td>1.53 ± 0.055</td>
<td>1.24</td>
<td>1.23 ± 0.014</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1-eicosanol</td>
<td>298.55</td>
<td>C\textsubscript{20}H\textsubscript{42}O</td>
<td>0.05</td>
<td>0.08 ± 0.043</td>
<td>2.09</td>
<td>1.67 ± 0.013</td>
<td>1.24</td>
<td>1.20 ± 0.018</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1-docosanol</td>
<td>326.6</td>
<td>C\textsubscript{22}H\textsubscript{46}O</td>
<td>0.05</td>
<td>0.09 ± 0.02</td>
<td>2.14</td>
<td>1.66 ± 0.055</td>
<td>1.37</td>
<td>1.26 ± 0.025</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1,2-tetradecanediol</td>
<td>230.39</td>
<td>C\textsubscript{12}H\textsubscript{22}O\textsubscript{2}</td>
<td>0.14</td>
<td>0.09 ± 0.02</td>
<td>2.14</td>
<td>1.66 ± 0.055</td>
<td>1.37</td>
<td>1.26 ± 0.025</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>pyrogluclid</td>
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<td>C\textsubscript{6}H\textsubscript{10}O\textsubscript{3}</td>
<td>0.90</td>
<td>0.46 ± 0.013</td>
<td>1.00</td>
<td>0.89 ± 0.103</td>
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<td>1.69 ± 0.015</td>
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</tr>
<tr>
<td></td>
<td>cholesterol</td>
<td>386.65</td>
<td>C\textsubscript{27}H\textsubscript{46}O</td>
<td>0.04</td>
<td>0.03 ± 0.002</td>
<td>1.70</td>
<td>1.28 ± 0.105</td>
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<td>1.14 ± 0.008</td>
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</tr>
<tr>
<td>carboxylic acid</td>
<td>decanoic acid</td>
<td>172.27</td>
<td>C\textsubscript{10}H\textsubscript{20}O\textsubscript{2}</td>
<td>0.20</td>
<td>0.21 ± 0.085</td>
<td>2.09</td>
<td>1.67 ± 0.027</td>
<td>1.43</td>
<td>1.41 ± 0.114</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>pentadecanoic acid</td>
<td>242.4</td>
<td>C\textsubscript{15}H\textsubscript{30}O\textsubscript{2}</td>
<td>0.13</td>
<td>0.08 ± 0.006</td>
<td>2.00</td>
<td>1.55 ± 0.103</td>
<td>1.34</td>
<td>1.23 ± 0.016</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>hexadecanoic acid</td>
<td>256.42</td>
<td>C\textsubscript{16}H\textsubscript{32}O\textsubscript{2}</td>
<td>0.13</td>
<td>0.13 ± 0.072</td>
<td>2.00</td>
<td>1.64 ± 0.338</td>
<td>1.33</td>
<td>1.31 ± 0.096</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>stearic acid</td>
<td>284.48</td>
<td>C\textsubscript{18}H\textsubscript{36}O\textsubscript{2}</td>
<td>0.11</td>
<td>0.14 ± 0.006</td>
<td>2.00</td>
<td>1.76 ± 0.075</td>
<td>1.32</td>
<td>1.33 ± 0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>oleic acid</td>
<td>282.46</td>
<td>C\textsubscript{18}H\textsubscript{36}O\textsubscript{2}</td>
<td>0.11</td>
<td>0.17 ± 0.005</td>
<td>1.78</td>
<td>1.50 ± 0.067</td>
<td>1.31</td>
<td>1.33 ± 0.108</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>glutaric acid</td>
<td>132.12</td>
<td>C\textsubscript{6}H\textsubscript{12}O\textsubscript{3}</td>
<td>0.80</td>
<td>0.61 ± 0.089</td>
<td>1.60</td>
<td>1.11 ± 0.071</td>
<td>2.20</td>
<td>1.90 ± 0.089</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>adipic acid</td>
<td>146.14</td>
<td>C\textsubscript{6}H\textsubscript{12}O\textsubscript{3}</td>
<td>0.67</td>
<td>0.69 ± 0.015</td>
<td>1.67</td>
<td>1.62 ± 0.052</td>
<td>2.03</td>
<td>2.06 ± 0.024</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15-hydroxypentadecanoic acid</td>
<td>258.42</td>
<td>C\textsubscript{15}H\textsubscript{30}O\textsubscript{2}</td>
<td>0.20</td>
<td>0.13 ± 0.083</td>
<td>2.00</td>
<td>1.11 ± 0.074</td>
<td>1.43</td>
<td>1.27 ± 0.075</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16-hydroxyhexadecanoic acid</td>
<td>272.43</td>
<td>C\textsubscript{16}H\textsubscript{32}O\textsubscript{2}</td>
<td>0.19</td>
<td>0.13 ± 0.064</td>
<td>2.00</td>
<td>1.28 ± 0.051</td>
<td>1.42</td>
<td>1.30 ± 0.073</td>
<td></td>
<td></td>
</tr>
<tr>
<td>carbohydrate</td>
<td>levoglucosan</td>
<td>162.14</td>
<td>C\textsubscript{6}H\textsubscript{12}O\textsubscript{3}</td>
<td>0.83</td>
<td>0.96 ± 0.074</td>
<td>1.67</td>
<td>1.23 ± 0.033</td>
<td>2.25</td>
<td>2.39 ± 0.098</td>
<td></td>
<td></td>
</tr>
<tr>
<td>amine</td>
<td>4-aminobenzoic acid</td>
<td>157.14</td>
<td>C\textsubscript{6}H\textsubscript{5}N\textsubscript{3}O\textsubscript{2}</td>
<td>0.29</td>
<td>0.13 ± 0.035</td>
<td>1.00</td>
<td>0.87 ± 0.016</td>
<td>0.14</td>
<td>0.11 ± 0.014</td>
<td>1.37</td>
<td>1.63 ± 0.058</td>
</tr>
<tr>
<td></td>
<td>quinone</td>
<td>324.42</td>
<td>C\textsubscript{6}H\textsubscript{5}N\textsubscript{3}O\textsubscript{2}</td>
<td>0.1</td>
<td>0.10 ± 0.096</td>
<td>1.20</td>
<td>1.35 ± 0.184</td>
<td>0.1</td>
<td>0.07 ± 0.044</td>
<td>1.33</td>
<td>1.35 ± 0.092</td>
</tr>
<tr>
<td>organic nitrate</td>
<td>3-methyl-4-nitrophenol</td>
<td>153.14</td>
<td>C\textsubscript{7}H\textsubscript{5}N\textsubscript{3}O\textsubscript{2}</td>
<td>0.43</td>
<td>0.46 ± 0.128</td>
<td>1.00</td>
<td>1.29 ± 0.128</td>
<td>0.14</td>
<td>0.11 ± 0.065</td>
<td>1.85</td>
<td>1.82 ± 0.104</td>
</tr>
<tr>
<td>anhydride</td>
<td>Carbon Dioxide</td>
<td>44.01</td>
<td>CO\textsubscript{2}</td>
<td>2</td>
<td>1.84 ± 0.005</td>
<td>3.67</td>
<td>3.45 ± 0.007</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.4 Elemental Analysis of Mixtures of Standard Organic Species

Previous sections demonstrate that the TOA-QMS is able to estimate organic elemental ratio and OM/OC reasonably accurate. Its performance is further tested with mixtures of organic species. More specifically, particle laden quartz-fiber filter punches with known organics were analyzed simultaneously with the TOA-QMS by placing one filter punch of each standard in the TOA-QMS at the same time. Table 6-4 shows the elemental analysis of mixtures of pure organic compounds, including a combinations of adipic acid, levoglucosan, stearic acid, and 1, 2 tetradecanediol. The raw atomic ratios were calibrated using the linear regression from the standard organic compounds. Differences in IE for each compound may create further uncertainties with respect to analysis of individual compounds (Aiken et al., 2007). Table 6-4 shows that the average absolute percent error for O/C, H/C, and OM/OC is 18.3%, 16.8% and 5.9%, respectively for organic standard mixtures. The average absolute percent error with HR-AMS for O/C and H/C is calculated at 10.55% and 8.65%. No data was provided for OM/OC. The accuracy and precision for the analysis of mixtures is similar to that of individual compounds.
Table 6-4. Elemental analysis of mixtures of pure organic compounds. Results are presented with \(\pm 1\sigma\) (standard deviation) and the absolute percent error.

<table>
<thead>
<tr>
<th>Compound</th>
<th>O/C</th>
<th>H/C</th>
<th>OM/OC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic</td>
<td>EA</td>
<td>% error</td>
</tr>
<tr>
<td>Adipic Acid + Levoglucosan</td>
<td>0.75</td>
<td>0.54± 0.019</td>
<td>-27.48</td>
</tr>
<tr>
<td>Stearic Acid + Levoglucosan</td>
<td>0.29</td>
<td>0.25± 0.000</td>
<td>-14.56</td>
</tr>
<tr>
<td>Adipic Acid + Levoglucosan + Stearic Acid</td>
<td>0.37</td>
<td>0.41± 0.044</td>
<td>11.42</td>
</tr>
<tr>
<td>Stearic Acid + Levoglucosan + 1,2 Tetradecanediol</td>
<td>0.24</td>
<td>0.28± 0.006</td>
<td>19.72</td>
</tr>
</tbody>
</table>

6.4 Elemental Analysis Application to Ambient Samples

The TOA-QMS was applied to measure O/C, H/C, and OM/OC ratios for the same Fresno samples used to analyze inorganic and organic species. The AMS suffers interferences from air peaks, especially for CO\(_2\), N\(_2\), H\(_2\)O, O\(_2\), and Ar when analyzing atmospheric aerosols in situ. The facts that TOA-QMS operates using ultrapure helium as the carry gas and the samples are dried before analysis reduce interferences and allow for fewer assumptions regarding ion signal intensities (Aiken et al., 2008).

Figure 6-5 shows the mass concentrations of NH\(_4^+\), SO\(_4^{2-}\), NO\(_3^-\), OM, and OC samples for the wintertime Fresno Supersite study collect between 12/15/2000 and 02/03/2001. Besides nighttime concentrations being higher for all species, especially OC and NO\(_3^-\), and the haze period demonstrate by the larger concentrations, a good reverse correlation between OC and OM/OC is observed (i.e., higher OC concentrations shows lower OM/OC values). The OM/OC average for this period is 2.55 ± 0.4 and is
representative of aged SOAs. Missing points represent data points which the O/C values were above two or H/C above four.

Figure 6-5. Mass concentrations for samples collected at the Fresno Supersite from 12/12/2000 and 02/03/2001. Good correlation between organics (organic carbon) and the OM/OC ratio can be observed. An increase in aerosol concentration can be observed for the periods between 12/27/2000 and 01/07/2001, where long periods of haze were reported.

Figure 6-6 shows the daily average inorganic, OC, O/C, H/C, and OM/OC. A relatively constant level of aerosol oxidation can be observed throughout the study period. The average O/C ratio was calculated to be $1.03 \pm 0.27$ while the H/C ratio was calculated to be $1.95 \pm 0.69$, which agrees with the high OM/OC observed. Higher values for H/C are observed from 12/15/2000 to 12/26/2000 where haze was not reported, while O/C remained fairly constant throughout the entire period.

The H/C varied from 0.88 to 3.86 with an average of 1.95 during this study period; O/C varied from 1.82 to 0.43 with an average of 1.03; N/C varied from 0.01 to 0.04 with
an average of 0.03. The OM/OC varied 1.73 to 3.72 with an average of 2.55. The average OC and OM concentrations are 8.55 and 21.21 µg/cm², respectively. Hence, the average conversion factor found from data analysis to determine OM concentration from OC concentration was calculated at 2.55 ± 0.4, which is higher than the conventionally used conversion factors of 1.4 or 1.8. This reflects the high contributions from biomass burning and aged aerosols.

![Graph](image_url)

Figure 6-6. O/C (red) and H/C (purple) ratios overlaid with inorganic and organic mass concentrations for samples collected at the Fresno Supersite from 12/15/2000 and 02/03/2001.

Morning (AM) and afternoon (PM) data were averaged and compared in Figure 6-7. H/C is the only value which is highest in the morning (7.2%), most likely due to the influence of primary hydrocarbon-like organic aerosols from local combustion-related emissions. It is not surprising that O/C and OM/OC are higher during the second part of the day as secondary organic aerosol formation is expected with increased
photochemistry reactions and since OM/OC is highly correlated to O/C. Figure 6-8 shows the direct correlation between O/C and OM/OC for all the Fresno Supersite wintertime data presented. This relationship is expected because of the high molecular mass of O, which significantly contributes to OM (Pang et al. 2006). This relationship has also been observed by Aiken et al. (2008) while applying the EA method with HR-AMS.

Figure 6-7. Average AM and PM aerosol concentration and EA ratios for data collected at the Fresno Supersite from 12/15/2000 to 02/03/2001.

Figure 6-8. Scatter plot of OM/OC vs O/C calculated from 58 ambient samples collected at the Fresno Supersite from 12/15/2000 to 02/03/2001.
Chapter 7: Conclusion

PM$_{2.5}$ mainly consists of NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, OC, EC and variable abundance of crustal elements. They originate from primary emissions as well as from gas-to-particle transformations in the atmosphere (Ravishankara, 1997). Studying the composition, concentration, and size-distribution of PM in the atmosphere is important for a better understanding of emission sources, transformation and transport processes, health and climate impacts, and assessment of policies (De Gouw and Jiminez, 2009; Simoneit et al., 1999).

Collection of atmospheric particles onto filter substrates is a common method for determining aerosol composition. Present off-line analytical methods for the analysis of organic and inorganic aerosols are largely based on solvent extraction; these procedures are costly and may require lengthy derivatization reactions (Chow, 1995; Chow et al., 2008; Grosjean, 1975; Novakov and Corrigan, 1995).

This study developed a TOA-QMS technique that couples a modified DRI model 2001 Thermal/Optical Carbon Analyzer to an electron ionization-quadrupole mass spectrometer to quantify both organic and inorganic aerosol fractions deposited on quartz-fiber filters in a single analysis.

To reduce interference from ambient air intrusion and background signal, the pressure of sample oven was set to 10 psi, and an argon sheath chamber pressurized at
7 psi was added to the sample loading area. The ambient air intrusion was reduced by 44.8%.

Once the system was optimized, TOA-QMS was calibrated with laboratory-generated \( \text{NH}_4^+, \text{NO}_3^-, \text{SO}_4^{2-} \), and oxalic acid aerosols to quantify the ionization efficiency (IE) and the relative ionization efficiency (RIE) of the TOA-QMS for inorganic and organic samples. These calculations allow for the comparison of mass concentration for samples analyzed at different periods of times, independent of system performance.

Fragmentation tables were developed to apportion ion signals to parent species in a procedure similar to that used to calibrate Aerodyne’s Aerosol Mass Spectrometer. \( \text{NH}_4^+, \text{NO}_3^-, \text{SO}_4^{2-} \), and organic species were individually accounted for in the mass spectra, and the mass concentration of each was calculated according to the ionization efficiency of each species. A correction factor was calculated for \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \), allowing for a more comparative analysis between the TOA-QMS with IC analysis.

Mass concentration of \( \text{NH}_4^+, \text{NO}_3^-, \text{SO}_4^{2-} \), and organics were calculated with the TOA-QMS for filter samples collected from the Fresno Supersite in the winter time during 2000-2001. TOA-QMS OC mass concentrations were compared to that by the DRI Model 2001 TOA, and \( \text{NH}_4^+, \text{NO}_3^-, \text{SO}_4^{2-} \) and concentrations were compared with IC analysis. Without the implementation of the correction factor, average mass concentration uncertainty varied from 1% to 28%. The lowest uncertainty was observed for the mass concentration of organic aerosols while the highest uncertainty was
observed for NO$_3^-$ and SO$_4^{2-}$ aerosols. Application of the correction factor reduced the average mass concentration uncertainty to a maximum of 6%. Analysis of time series of the Fresno Supersite aerosols shows that the TOA-QMS can track the temporal changes of each species, making it a potential technique to analyze aerosol samples collected over wide spatial and temporal scales.

Additional experiments were performed in order to test the ability of the TOA-QMS to estimate the O/C, H/C, N/C, and the OM fractions in ambient aerosols. Calibration of the TOA-QMS for elemental analysis was conducted using 21 selected organic compounds containing different nominal ratios. O/C, H/C, and N/C. TOA-QMS calibration coefficients were determined to be (0.93x ± 0.036) for O/C, (0.77x ± 0.06) for H/C, (0.75x ± 0.06) for N/C, and ((0.94 ± 0.043)x + 0.034) for OM/OC.

Elemental analysis was applied to the Fresno Supersite samples and the O/C, H/C, and OM/OC ratios were derived. Although the quantification of N/C fraction of the aerosol was explored, more points are necessary for a more robust calibration correction factor. Good correlations are found between organic carbon, inorganic species, OM concentrations, O/C, and OM/OC. In addition, separation of the data into morning and afternoon periods shows that H/C is highest in the morning, while O/C and OM/OC are higher during the second part of the day.

The TOA-QMS provides unique capability to analyze NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$ and OC concentrations in aerosol samples, and allows for the estimation of O/C, H/C, N/C, and
OM/OC ratios. It removes the need for analyzing the same filter by different techniques, thus reduces analysis costs and time. This data provides new information on the particle composition and properties.

The TOA-QMS system can be further improved by adding a seven wavelength optical system to measure the particle optical properties (Chen et al., 2015; Chow et al., 2015b). Information from this system may be applied to source apportionment for black and brown carbon, association of optical properties with specific organic compounds, ground-truthing of multi-spectra remote sensors, and improvement on Earth’s radiation balance estimates.
Appendix A

Argon Sheath Design and Specifications

Figure A-1. Argon sheath design and specifications.
Figure A-2. Argon sheath design and specifications
Temperature Calibration Curve

Figure A-3. Temperature calibration curve obtained with a NIST certified thermocouple compared to the TOA thermocouple. The equation of the line is inserted into the TOA software and used to correctly heat the sample oven according to the protocol.
Example of Mass Spectra with and without the argon sheath

Figure A-4. Example of a sample analyzed with and without the argon sheath chamber. Note that when the argon sheath chamber was not used a negative peak at m/z 32 is observed. This indicates that the oxygen present in the TOA-QMS was used as an oxidant. Also note the larger peak at m/z 44. The available oxygen in the system most likely was used to form CO₂ by oxidizing CO. A much larger CO peak m/z 28 is observed when the argon sheath chamber was used.
Appendix B

Program Code for Normalization, Subtraction, and LOD Values.

The algorithm for CompleProgram_Final.m is the following:

1) From the 3D data extracted from the sample mass spectrum, determine a starting baseline point for steps 1, 2, and 3 by averaging 20 points before the TOA starts to ramp its temperature.

2) Calculates the area under the peaks for temperature steps 1, 2, and 3, starting from point zero. Since each temperature step lasts 600 seconds, peak areas are calculated for 600 seconds once the TOA sample oven temperature set point increases.

3) Calculates the area of ion signal between the baseline and the zero point (i.e. the area of a rectangle). The rectangle will have a width that represents 600 seconds and a height from point zero to the baseline point found in step 1.

4) Subtracts the area of the rectangle found in step 3 from the area of the curve calculated in step 2.

5) Calculates the area of the calibration peak by summing the peak areas of CO$_2$ fragments at m/z 12, 22, 28, 29, 16, 45, and 46 by following the same procedure as in steps 2 and 3. The width of the rectangle will represent 5 minutes. CO$_2$ is injected into the TOA-QMS after the last temperature step is finished (i.e. 35 minutes into the analysis).
6) The area of each peak for each ion found in step 1, step 2, and step 3 are divided by the area of the calibration peak. One special calculation is done for \(m/z\) 18 (\(\text{H}_2\text{O}\)) since its baseline has been observed to drift with time. Hence, the area of the peak calculated from the zero point is subtracted by the area found by half of the height of the baseline for step 1 plus half of the height of the baseline for step 2 in 600 seconds. This method minimizes underestimating the height of the peak. The reason this is only applied to \(\text{H}_2\text{O}\) at this time is because the code would have to be manually entered for 450 points, making it unreasonably long and unnecessary, as it will be observed in comparison analysis in Chapter 4.

7) Blank quartz-fiber filter data, which have also been normalized by the previous steps, are averaged.

8) Averaged blank quartz-fiber filter data is subtracted from user selected data files.

9) An Excel file is created for each sample data selected. Files are written with the extension _SUB. A prompt appears and asks if the user wishes to calculate the limit of detection by using normalized blank quartz-fiber filter data. Selecting YES will prompt the user to select the folder containing blank files. Data in the blank files will be averaged and the standard deviation will be calculated. The limit of detection is calculated for each ion from the average and the standard deviation values with the equation \(\text{LOD} = \text{AVERAGE} + 3 \times \text{STANDARD}\)
DEVIATION. Selecting NO will prompt the user to select a file with the limits of detection for each ion already calculated.

10) Once the limit of detection file is created and/or selected, the program will ask the user to select the folder where the files he desires to apply the limit of detection can be found.

11) Sample data is then compared to the limit of detection. Sample data values below the detection limit values will be reported as zero.

12) The program will create a file with extension _DETLIM.

%This program calculates peak areas obtained from 3D data exported from the mass spectrum of analyzed samples, performs blank subtractions, and presents the data adjusted with the detection limit for each ion.

%THIS PROGRAM DETERMINES THE BASELINE FOR A CHROMATOGRAM OBTAINED WITH THE TDMS 3STEP PROGRAM FOR THE INDIVIDUAL STEP TIMES, INTEGRATES THE PEAKS THAT ARE PRESENT IN THE TIME RANGE, and SUBTRACT BLK FILES FROM THE MAIN SAMPLE FILE. SUBTRACTED AND NORMALIZED DATA ARE THEN LIMITED BY THE USER'S LIMIT OF DETECTION FILE THAT IS CALCULATED BY THIS PROGRAM AS WELL. A FINAL FILE IS CREATED IN .XLS FORMAT. COLUMNS 1-3 SHOW DATA FOR STEPS 1, 2, AND 3 RESPECTIVELY. COLUMN 4 SHOWS THE SUM OF THE STEPS.

%Blank files must be place in the same folder as the sample file.
% Files must be prepared by deleting the headings first, and the count number. A new folder will be created with the new file containing the normalization and the subtraction. Sample files must have prefix sdk and blank files must have prefixes blk. SEE LINE 121 and 147 for prefixes changes. Normalized files will have a suffix "_new" normalized and subtracted files will have suffix "_SUB"
%% Normalize raw files

waitfor(msgbox('Select Folder Containing Raw Sample Data Files'));

Main_Directory = uigetdir('C:\Users\griggio\Desktop\Thesis Material\Organic Standard\!2015');
newfolder=strcat(Main_Directory, '\','NormalizedData');

% -----------Turn the files in directory into list----------------------
New_Directory=ls(Main_Directory); %grabs all the file names and puts it in char variable
New_Directory=New_Directory(3:length(New_Directory(:,1)),:); %removes the
% '.' and '..' from the folder
%-----------------Loop through files---------------------------------------
fprintf('size :%d', size(New_Directory));
for i = 1:size(New_Directory)
    fprintf('Normalizing and Subtracting file: %d
',i);

%-----Load Data file in folder-------------------------------------------
data=load(strcat(Main_Directory,'/',New_Directory(i,:)));

%---------Continue with the Program--------------------------------------(Xufei's program)

z=nan(1,491);
% Data for steps 1 through 4
OC1=data([258:773],[1:441]);
OC2=data([774:1288],[1:441]);
OC3=data([1289:1803],[1:441]);
OC4=data([1808:2066],[1:441]); %new
% Peak area for steps 1 through 4 = sum of points
OC1S=sum(OC1);
OC2S=sum(OC2);
OC3S=sum(OC3);
OC4S=sum(OC4);

% Baseline values for steps 1 through 4
OCB1list=data([238:257],[1:441]);
OCB2list=data([754:773],[1:441]);
OCB3list=data([1269:1288],[1:441]);
OCB4list=data([1783:1802],[1:441]);
OCB4H2O=data([1783:1803],[1:441]);

% Average of the baseline points
OCB1=mean(OCB1list);
OCB2=mean(OCB2list);
OCB3=mean(OCB3list);
OCB4=mean(OCB4list);
OCB4H2O=mean(OCB4H2O);

% List of values for water peak only
H2OOC1B=OCB1(9);
H2OOC2B=OCB2(9);
H2OOC3B=OCB3(9);
H2OOC4B=OCB4H2O(9);
H2OOC1S=OC1S(9)-515*(0.5*H2OOC1B+0.5*H2OOC2B);
H2OOC2S=OC2S(9)-515*(0.5*H2OOC2B+0.5*H2OOC3B);
H2OOC3S=OC3S(9)-515*(0.5*H2OOC3B+0.5*H2OOC4B);

% Peak area minus the baseline value for each step
OC1S=OC1S-515*OCB1;
OC2S=OC2S-515*OCB2;
OC3S=OC3S-515*OCB3;
OC4S=OC4S-258*OCB4;
OC1S(9)=H2OOC1S;
OC2S(9)=H2OOC2S;
OC3S(9)=H2OOC3S;
%OC1S(OC1S<0)= 0;
%---------- Normalization TIC Calculation -----------------------

CO2=data(1808:2066,35); \%44

c = sum(CO2);

c = c-258*OCB4(35); \% sum of CO2 - 5min(258)*baseline

z(1,1)= c;

N2=data([1808:2066],19); \%28
d = sum(N2);
d = d-(258*OCB4(19));

TwentyNine=data([1808:2066],20); \%29
m = sum(TwentyNine);
m = m-258*OCB4(20);

TT=data([1808:2066],13); \%TT = ion 22
e = sum(TT);
e = e-258*OCB4(13); \%22

O=data([1808:2066],7); \%16
f = sum(O);
f = f-258*OCB4(7);

Carbon=data([1808:2066],3); \%12
g = sum(Carbon);
g = g-258*OCB4(3);

FV=data([1808:2066],36); \% ion 45
h = sum(FV);
h = h-258*OCB4(36);

FS=data([1808:2066],37); \% ion 46
j = sum(FS);
j = j-258*OCB4(37);

k = c+d+e+f+g+h+j+m;

z(1,2)= k;
% R = c/k;
% z(1,3) = R;

aa=[10:450]; %Insert count from 10 to 450

%--------Concatenate values and put into rows-------------------
OCS = [aa',OC1S',OC2S',OC3S',aa', (OC1S/k)',(OC2S/k)',(OC3S/k)'];

%--------Write Data -----------------------------------------------
if ~(isdir(newfolder)) % checks for folder called NewBaselineData
    mkdir(newfolder); % if folder doesnt exist create folder NewBaselineData
end

cd (newfolder); %Enter newfolder called NewBaselineData

%dlmwrite([strtrim(New_Directory(i,:)) '_Normalized'], OCS);
end

%------------------------------------------------------------------

% Enter Subtraction Program

%------Enter NewBaselineData folder to do Blank subtraction--------

%---------Loops through files in NewBaselineData folder----------
%for j = 1:length(New_BLKDir(:,1));
%fprintf('Now on BLK j=%d
',j);
%---------Assigns blank arrays to be overwritten on next step--------
array1=nan(441,5);
array2=nan(441,5);
array3=nan(441,5);

%----------Loops through files starting with BLK---------------------
fn3=ls('blk*');  % grabs all the file names and puts it in char variable
for l = 1:length(fn3(:,1))
    fprintf('Now subtracting collumn =%d\n',l);
    %------Loads BLKs and assign to read colllums 6,7,8------------------
    blank = load(fn3(l,:));
    col1 = blank(:,6);
    col2 = blank(:,7);
    col3 = blank(:,8);
    %---Places BLKs into array and replace the empty arrays created
    % above
    array1(:,l)=col1;
    array2(:,l)=col2;
    array3(:,l)=col3;
end

clear blank

%----------Average the arrays from index 2 (by column)--------------
%-----The maximum blanks here is 4-----More than 4 will not work-----
array1(:,5)=nanmean(array1(:,1:4),2);
array2(:,5)=nanmean(array2(:,1:4),2);
array3(:,5)=nanmean(array3(:,1:4),2);

%----------Gets file starting with SDK and loads it--------------
fn4=ls('SDK*');  % change extention to match your file
for bb=1:length(fn4(:,1))
    sample=load(fn4(bb,:));
    %--------Creates a NAN 'file' with 491 rows and 4 colllums--------
sample2=nan(441,4);
%--------First column is assigned to display from 10 to 500------
sample2(:,1)=[10:450];

%----Subtract the averaged BLK files from the SDK file according to the right column
sample2(:,2)=sample(:,6)-array1(:,5);
sample2(:,3)=sample(:,7)-array2(:,5);
sample2(:,4)=sample(:,8)-array3(:,5);

%--Writes a new file with extension _SUB into NewBaselineData folder

dlmwrite([strtrim(fn4(bb,:)) '_SUB'], sample2)%writes ASCII file
%xlswrite([strtrim(fn4(bb,:)) '_SUB'], sample2)%writes Excel file
end
%end

cd ('C:\Users\grigio\Desktop\Thesis Material\Organic Standard\!2015');
clear all
%-----------------------------------------------
% Select folder containing blank files that will be used to calculate the limit of detection (LOD). Blank files need to not have heading and number column - much like the blank files used for subtraction.
%-----------------------------------------------

button = questdlg('Calculate the Limit of Detection (LOD) from Blank Files?');
if strcmp(button,'Yes')
    waitFor(msgbox('Select Folder Containing Blank Files for LOD Calculation.'));
end
cd ('C:\Users\griggio\Desktop\Thesis Material\Organic Standard\!2015');
Blank_Directory = uigetdir;
cd(Blank_Directory);
Blankfolder=strcat(Blank_Directory, '\', 'Normalized_BLKs');

%------------------------Turn the files in directory into list------------------------
NewBlank_Directory=ls(Blank_Directory); % grabs all the file names and puts it in char variable
NewBlank_Directory=NewBlank_Directory(3:length(NewBlank_Directory(:,1)),:); % removes the '.' and '..' from the folder
%----------------------------------Loop through files----------------------------------
%fprintf('size :%d', size(New_Directory));
for i = 1:size(NewBlank_Directory)
    fprintf('Normalizing Blank File: %d
',i);

%--------------------------------Load Data file in folder--------------------------------
data=load(strcat(Blank_Directory, '/'), NewBlank_Directory(i,:));

%--------------------------------Continue with the Program--------------------------------
z=nan(1,491);
% Data for steps 1 through 4
OC1=data([258:773],[1:441]);
OC2=data([774:1288],[1:441]);
OC3=data([1289:1803],[1:441]);
OC4=data([1808:2066],[1:441]);

% Peak area for steps 1 through 4 = sum of points
OC1S=sum(OC1);
OC2S=sum(OC2);
OC3S=sum(OC3);
OC4S=sum(OC4);
% Baseline values for steps 1 through 4
OCB1list=data([238:257],[1:441]);
OCB2list=data([754:773],[1:441]);
OCB3list=data([1269:1288],[1:441]);
OCB4list=data([1783:1802],[1:441]);
OCB4H2O=data([1783:1803],[1:441]);

% Average of the baseline points
OCB1=mean(OCB1list);
OCB2=mean(OCB2list);
OCB3=mean(OCB3list);
OCB4=mean(OCB4list);
OCB4H2O=mean(OCB4H2O);

% List of values for water peak only
H200C1B=OCB1(9);
H200C2B=OCB2(9);
H200C3B=OCB3(9);
H200C4B=OCB4H2O(9);
H200C1S=OC1S(9)-515*(0.5*H200C1B+0.5*H200C2B);
H200C2S=OC2S(9)-515*(0.5*H200C2B+0.5*H200C3B);
H200C3S=OC3S(9)-515*(0.5*H200C3B+0.5*H200C4B);

% peak area minus the baseline value for each step
OC1S=OC1S-515*OCB1;
OC2S=OC2S-515*OCB2;
OC3S=OC3S-515*OCB3;
OC4S=OC4S-258*OCB4;
OC1S(9)=H200C1S;
OC2S(9)=H200C2S;
OC3S(9)=H200C3S;
OC1S(OC1S<0)= 0;

%------------- Normalization TIC Calculation
CO2 = data(1808:2066,35); %44

% sum of CO2 - 5min(258)*baseline
z(1,1) = c;

N2 = data([1808:2066],19); %28

m = sum(TwentyNine);

m = m-258*OCB4(20);

TT = data([1808:2066],13); %TT = ion 22
f = sum(O);

f = f-258*OCB4(7);

FV = data([1808:2066],36); % ion 45

h = sum(FV);

h = h-258*OCB4(36);

FS = data([1808:2066],37); % ion 46

j = j-258*OCB4(37);

k = c+d+e+f+g+h+j+m;

z(1,2) = k;

% R = c/k;

% z(1,3) = R;

aa=[10:450]; %Insert count from 10 to 450
%-------Concatenate values and put into rows------------------------
OCS = [aa', (OC1S/k)', (OC2S/k)', (OC3S/k)'];
%-------Write Data ----------------------------------------------------
if ~(isdir(Blankfolder)) % checks for folder called NewBaselineData
mkdir(Blankfolder); % if folder doesnt exist create folder
NewBaselineData
end
cd (Blankfolder); %Enter newfolder called NewBaselineData
%Write new file into NewBaselineData with suffix _New
dlwrite([strtrim(NewBlank_Directory(i,:)) '_Normalized'], OCS);
end
%
%-------Enter Normalized_BLKs folder to do Blank averages------------

cd (Blankfolder); %Enter newfolder called NewBaselineData
New_BLKDir=ls; %grabs all the file names and puts it in char variable
New_BLKDir=New_BLKDir(3:length(New_BLKDir(:,1)),:); %removes the '.' and '..' from the previous char var

fn=ls(Blankfolder); %grabs all the file names and puts it in char variable
fn=fn(3:size(fn,:),:); %removes the '.' and '..' from the previous char var
build1=size(fn(:,1));
build=build1(1);

%-------Assigns blank arrays to be overwritten on next step--------
% Arrays assigned to 450 rows (i.e 441) for blks
array4=nan(441,build+1);
array5=nan(441,build+1);
array6=nan(441,build+1);

% Arrays assigned to 450 rows (i.e. 441) for std dev
array7=nan(441,build+1);
array8=nan(441,build+1);
array9=nan(441,build+1);

%-------------------Loop through files-----------------------------
for i = 1:size(fn)

    fprintf('Calculating Average and Standard Deviation: %d\n',i);

%-------- Loads BLKs and assign to read columns 1, 2, 3 ---------
    blank = load(fn(i,:));
    col4 = blank(:,2);
    col5 = blank(:,3);
    col6 = blank(:,4);
    col7 = blank(:,2);
    col8 = blank(:,3);
    col9 = blank(:,4);

%---Places BLKs into array and replace the empty arrays created
% above for averaging blanks
    array4(:,i)=col4;
    array5(:,i)=col5;
    array6(:,i)=col6;

%---Places BLKs into array and replace the empty arrays created
% above for standard deviation of blanks
    array7(:,i)=col7;
    array8(:,i)=col8;
    array9(:,i)=col9;

    %--Add columns of the array used for averaging blanks and sums the
    % rows
    clear blank
end

%-------Average the arrays from index 2 (top - down)----------
%------The maximum blanks here is 4---More than 4 will not work------
array4(:,build+1)=nanmean(array4(:,,:),2);
array5(:,build+1)=nanmean(array5(:,,:),2);
array6(:,build+1)=nanmean(array6(:,,:),2);

%-------Standard deviation of the arrays from index 2 (top - down)-----
%------The maximum blanks here is 4---More than 4 will not work------
array7(:,build+1)=nanstd(array7(:,,:),0,2);
array8(:,build+1)=nanstd(array8(:,,:),0,2);
array9(:,build+1)=nanstd(array9(:,,:),0,2);

%-------Creates a NAN 'file' with 491 rows and 4 columns for blks-----
avg=nan(441,4);
avg(:,1)=10:450; %First column is assigned to display from 10 to 500
avg(:,2)=array4(:,build+1);
avg(:,3)=array5(:,build+1);
avg(:,4)=array6(:,build+1);

%-------Creates a NAN 'file' with 491 rows and 4 columns for stdev-----
stdev=nan(441,4);
stdev(:,1)=[10:450]; %First column is assigned to display from 10 to 500
%-------Places stdev into column 6,7,8--------
stdev(:,2)=array7(:,build+1);
stdev(:,3)=array8(:,build+1);
stdev(:,4)=array9(:,build+1);
%---Multiply standard deviation values by 3 ------------------------
threestdev=nan(441,4);

threestdev(:,1)=[10:450]; %First collumn is assigned to display from 10 to 500

threestdev(:,2)=3*array7(:,build+1);

threestdev(:,3)=3*array8(:,build+1);

threestdev(:,4)=3*array9(:,build+1);

%--Add average value of blanks to 3*standard deviation(LOD=BlkAvg+3*STDEV--

LOD=nan(441,4);

LOD(:,1)=[10:450]; %First collumn is assigned to display from 10 to 500

LOD(:,2)= avg(:,2)+threestdev(:,2);

LOD(:,3)= avg(:,3)+threestdev(:,3);

LOD(:,4)= avg(:,4)+threestdev(:,4);

%---Combine blk avg, stdev, 3*stdev, and LOD data in one file-------

C = cat(2,avg,stdev,threestdev,LOD);

%--Writes a file into Normalized_BLKs folder 'C' from line (434) above-

%xlsxwrite('BLK_STDEV_3STDEV_LOD',C); %writes Excel file

%dlmwrite('BLK_STDEV_3STDEV_LOD',C); %writes ASCII file

dlmwrite('LOD',LOD); %writes ASCII file

%

%------------------------------------------------------------------------------------------------------

%   Returns to file with samples to be compared to LOD

%------------------------------------------------------------------------------------------------------

cd ..

waitfor(msgbox('Click OK to Select LOD File'));

cd('C:\Users\griggio\Desktop\Thesis Material\Organic Standard\!2015')

[LOD_File,LOD_Path] = uigetfile('*.*');

cd(LOD_Path);

LOD_load = load(LOD_File);
% Select Directory where files that have been normalized and subtracted
% from blank files. These files will be compared to the LOD file.
% values below the LOD will be shown as ZERO, while values above the
% LOD will remain the same.

% Asks user to select directory where normalized and subtracted files are
waitfor(msgbox('Select Directory Containing Files to be Compared to the
LOD Values'));

% Opens window for directory to be selected
SampleFile_Directory = uigetdir;

% Creates folder named LOD_Data
newfilefolder=strcat(SampleFile_Directory,'\','LOD_Data');

% Grabs all the file names and puts it in char variable
NewFile_Directory=ls(SampleFile_Directory);

%removes the '.' and '..' from the folder

% Goes to directory with the chosen files
cd(SampleFile_Directory);

%--------Assigns blank arrays to be overwritten on next step--------
array1=nan(441,4);
array2=nan(441,4);
array3=nan(441,4);
step1=nan(441,4);
step2=nan(441,4);
step3=nan(441,4);

for m = 1:length(LOD_load(:,1))
    Final_col1 = LOD_load(:,2);
    Final_col2 = LOD_load(:,3);
    Final_col3 = LOD_load(:,4);
end

%---Places LOD into array and replace the empty arrays created above----
array_LOD1(:,1)=Final_col1;
array_LOD2(:,2)=Final_col2;
array_LOD3(:,3)=Final_col3;
end

fn5=ls('*_SUB'); %Gets files with SUB at the end

for bb = 1:length(fn5(:,1));
    fprintf('Generating Final File :%d
',bb);
    Final_sample=load(fn5(bb,:));
end

%--------Creates a NAN 'file' with 491 rows and 4 columns--------
step1 = Final_sample(:,2);
step2 = Final_sample(:,3);
step3 = Final_sample(:,4);

%---Places BLKs into array and replace the empty arrays created above
array1a(:,1)=step1;
array2a(:,2)=step2;
array3a(:,3)=step3;

%----Subtract the averaged BLK files from the SDK file according
to the right column

step1(step1 < Final_col1)= 0;
step2(step2 < Final_col2)= 0;
step3(step3 < Final_col3)= 0;
sample3(:,1) = 10:450;
sample3(:,2)=step1;
sample3(:,3)=step2;
sample3(:,4)=step3;

BlkArraySum = nan(441,2);
BlkArraySum(:,1)= 10:450;
%SumBlkArray=nan(441,2);
%SumBlkArray(:,1)= 10:450;
for Final_j = 1

    Final_col8=step1(:,1);
    Final_col9=step2(:,1);
    Final_col10=step3(:,1);

    BlkArraySum(:,2)=Final_col8+Final_col9+Final_col10;
    % SumBlkArray(:,)=BlkArraySum;

    C = cat(2,sample3,BlkArraySum);
end

%writes Excel file
if ~(isdir(newfilefolder))
    % if folder doesn't exist create folder LOD_Data
    mkdir(newfilefolder);
end

cd (newfilefolder);

xlswrite([strtrim(fn5(bb,:)) '_DETLIM'], C)

cd ..
end

else
  %-------------------------------------------------------------------
  %         Returns to file with samples to be compared to LOD
  %-------------------------------------------------------------------

  waitfor(msgbox('Click OK to Select LOD File'));
  cd ('C:\Users\griggio\Desktop\Thesis Material\Organic Standard\!2015\BLKs\Normalized_BLKs\LIM_DETECTION')
  [LOD_File1,LOD_Path1] = uigetfile('*.');
  cd(LOD_Path1);
  LOD_load1 = load(LOD_File1);
  %LOD/File = uigetfile ('*.');
  %LOD_load = load(LOD_File);

  % Select Directory where files that have been normalized and subtracted
  % from blank files. These files will be compared to the LOD file.
  % values below the LOD will be shown as ZERO, while values above the
  % LOD will remain the same.
% Asks user to select directory where normalized and subtracted files are
waitfor(msgbox('Select Directory Containing Files to be Compared to the LOD Values'));

cd ('C:\Users\griggio\Desktop\Thesis Material\Organic Standard\!2015');
% Opens windown for directory to be selected
SampleFile_Directory1 = uigetdir;
% Creates folder named LOD_Data
newfilefolder=strcat(SampleFile_Directory1,'\','LOD_Data');
% Grabs all the file names and puts it in char variable
NewFile_Directory=ls(SampleFile_Directory1);
%removes the '.' and '..' from the folder
% Goes to directory with the chosen files
cd(SampleFile_Directory1);
%--------Assigns blank arrays to be overwritten on next step--------
array1=nan(441,4);
array2=nan(441,4);
array3=nan(441,4);
step1=nan(441,4);
step2=nan(441,4);
step3=nan(441,4);
for m = 1:length(LOD_load1(:,1))
    Final_col1 = LOD_load1(:,2);
    Final_col2 = LOD_load1(:,3);
    Final_col3 = LOD_load1(:,4);
```matlab
%---Places LOD into array and replace the empty arrays created above----
array_LOD1(:,1)=Final_col1;
array_LOD2(:,2)=Final_col2;
array_LOD3(:,3)=Final_col3;
end

fn5=ls('*_SUB'); %Gets files with SUB prefixex

for bb = 1:length(fn5(:,1));
    fprintf('Generating Final File :%d\n',bb);
    Final_sample=load(fn5(bb,:));
    %--------Creates a NAN 'file' with 491 rows and 4 columns--------
    step1 = Final_sample(:,2);
    step2 = Final_sample(:,3);
    step3 = Final_sample(:,4);

    %---Places SUBs into array and replace the empty arrays created above----
    array1a(:,1)=step1;
    array2a(:,2)=step2;
    array3a(:,3)=step3;
    %--Compares Sub files with LOD File by column
    step1(step1 < Final_col1)= 0;
    step2(step2 < Final_col2)= 0;
    step3(step3 < Final_col3)= 0;
    sample3(:,1) = 10:450;
    sample3(:,2)=step1;
    sample3(:,3)=step2;
    sample3(:,4)=step3;
```
BlkArraySum = nan(441,2);
BlkArraySum(:,1)= 10:450;
%SumBlkArray=nan(441,2);
%SumBlkArray(:,1)= 10:450;
for Final_j = 1
    Final_col8=step1(:,1);
    Final_col9=step2(:,1);
    Final_col10=step3(:,1);

    BlkArraySum(:,2)=Final_col8+Final_col9+Final_col10;
    % SumBlkArray(:,)=BlkArraySum;
    C = cat(2,sample3,BlkArraySum);
end

%writes Excel file
if ~(isdir(newfilefolder))
    % if folder doesnt exist create folder LOD_Data
    mkdir(newfilefolder);
end

    cd (newfilefolder);
    xlswrite([strtrim(fn5(bb,:)) '_DETLIM'], C)
    cd ..;
end

waitfor(msgbox('Program Finished'));
end

clear all;
Program Code for Calculation Inorganic and Organic Aerosol Fractions.

The following program applies the fragmentation table to sample data obtained with the EI-MS.

Refer to chapter 3 for more information.

The algorithm for INORGANIC_CONC.m is the following:

1) The program asks the user to select the sample file to be analyzed

2) The program asks the user to select the file containing the \( \text{NH}_4^+ \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), and organic fragmentation pattern files in the respective order. Note that fragmentation pattern files must be in Excel format. Every time a fragmentation pattern file is selected the program calculates the corresponding ion signal.

3) Organic signals are calculated by subtraction of inorganic signals at each m/z (see Chapter 4 for a more detailed explanation of the fragmentation table).

4) Once all calculations are done the program prompts the user to save the file.

5) An Excel file containing the concentrations of \( \text{NH}_4^+ \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), and OC is created.

% This program calculates the concentration of Ammonium, Sulfate, Nitrate, and Organic Carbon from air samples collected with quartz-fiber filters.

% Samples must have already been normalized and run through the 'CompleteProgram_Final.m' program. CompleteProgram_Final will create a file containing 6 columns. This program gets the 6th columns and perform analysis on that data. i.e., ONLY NUMBERS ON THE 6TH COLUMN ARE ANALYZED.

% The program uses values from the fragmentation table to calculate the
% concentrations as well. These values are found in excel sheets created by the
% user. The location of these files are currently at
% 'C:\Users\griggio\Desktop\Thesis Material\Frag Table'.
% Asks user to select folder containing the sample file that is to be
% analyzed for the concentration of ammonium, sulfate, nitrate, and OC.
waitfor(msgbox('This Program Calculates Inorganic Concentrations'));

% Open the browsing window in this path
cd('C:\Users\griggio\Desktop\Thesis Material\Organic Standard\!2015')

% Tell user what to select. i.e., select det lim file to be analyzed
waitfor(msgbox('Click OK to Select the Sample File to be Analyzed'));

% Set the selected file to be named DetLim_File and set path as
% Det_Path
[DetLim_File,Det_Path] = uigetfile('*.*');

% Goes to the Det_Path
cd(Det_Path);
% Loads the DetLim_File
DetLim_load = xlsread(DetLim_File);
% Set a new folder to be created named Inorganic Concentration
newfolder=strcat(Det_Path,'\', 'Inorganic Concentration');

%------------Turn the files in directory into list----------------------
% Grabs all the file names and puts it in char variable
New_Directory=ls(Det_Path);
% Removes the '.' and '..' from the folder
New_Directory=New_Directory(3:length(New_Directory(:,1)),:);
% Goes to directory with the chosen files
cd(Det_Path);

format long;
for m = 1:length(DetLim_load(:,1))
    Final_col1 = DetLim_load(:,6);

    %--- Places LOD into array and replace the empty arrays created above----
    array_DetLim1(:,1)=Final_col1;
end

Punch = 0.53;

%--=--------------------------------------------------------------------
%--=--------------------------------------------------------------------
waitfor(msgbox('Click OK to Select the NH3 Frag. Table File'));

% Opens Ammonia Frag. Table File
[ NH3_File,NH3_Path ] = uigetfile('*.*');
cd(NH3_Path);
Ammonia = xlsread(NH3_File);
% Set Frag. Table positions for each m/z
NH_Slope = Ammonia(1,2);
NH_14 = Ammonia(2,2);
NH_15 = Ammonia(3,2);
NH_16 = Ammonia(4,2);
NH_17 = Ammonia(5,2);
%---------------------------------------------------------------------
%---------------------------------------------------------------------

waitfor(msgbox('Click OK to Select the Nitrate Frag. Table File'));
cd('C:\Users\griggio\Desktop\Thesis Material\Frag Table')
% Opens Nitrate Frag. Table File
[Nitrate_File,Nitrate_Path] = uigetfile('*.*');
cd(Nitrate_Path);
Nitrate = xlsread(Nitrate_File);
% Set Frag. Table positions for each m/z
Nitrate_Slope = Nitrate(1,2);
NO_14_30 = Nitrate(2,2);
NO_14_46 = Nitrate(2,3);
NO_30 = Nitrate(3,2);
NO_31 = Nitrate(4,2);
NO_32 = Nitrate(5,2);
NO_44_30 = Nitrate(6,2);
NO_44_46 = Nitrate(6,3);
NO_46 = Nitrate(7,2);
NO_47 = Nitrate(8,2);
NO_48 = Nitrate(9,2);
%---------------------------------------------------------------------
%---------------------------------------------------------------------

waitfor(msgbox('Click OK to Select the Sulfate Frag. Table File'));

cd('C:\Users\griggio\Desktop\Thesis Material\Frag Table')
% Opens Nitrate Frag. Table File
[Sulfate_File,Sulfate_Path] = uigetfile('*.*');
cd(Sulfate_Path);
Sulfate = xlsread(Sulfate_File);

% Set Frag. Table positions for each m/z
Sulfate_Slope = Sulfate(1,2);
SO_48 = Sulfate(2,2);
SO_64 = Sulfate(3,2);

%---------------------------------------------------------------------
%---------------------------------------------------------------------

waitfor(msgbox('Click OK to Select the Organic Frag. Table File'));
cd('C:\Users\griggio\Desktop\Thesis Material\Frag Table')

% Opens Nitrate Frag. Table File
[Organic_File,Organic_Path] = uigetfile('*.*');

cd(Organic_Path);
Organic = xlsread(Organic_File);

% Set Frag. Table positions for each m/z
Org_Slope = Organic(1,2);
Org_30 = Organic(2,2);
Org_48 = Organic(3,2);
Org_64 = Organic(3,2);

%---------------------------------------------------------------------
% Set sample fragments to match same name convention used in frag table
% Ex. m/z 14 for nitrate is called frag_nitrate[14]
% Numbers are spelled out
% Just to make things easier to follow
%---------------------------------------------------------------------

% Ammonia
Fourteen = Final_col1(5,1); % Also used for Nitrate
Fifteen = Final_col1(6,1);
Sixteen = Final_col1(7,1);
Seventeen = Final_col1(8,1);

% Nitrate
Thirty = Final_col1(21,1);
ThirtyOne = Final_col1(22,1);
ThirtyTwo = Final_col1(23,1);
FortySix = Final_col1(37,1);
FortySeven = Final_col1(38,1);
FortyEight = Final_col1(39,1); % Also used for Sulfate

% Sulfate
SixtyFour = Final_col1(55,1);

% Water
Eighteen = Final_col1(9,1);

% Organic
TwentyNine = Final_col1(20,1);
Fifty = Final_col1(41,1);
SixtyTwo = Final_col1(53,1);
SeventyEight = Final_col1(69,1);

% CO2
FortyFour = Final_col1(35,1);
FortyFive = Final_col1(36,1);

%----------------------------------------------------------
%                         Iterations
%----------------------------------------------------------
%----------------------------------------------------------
% Ammonia m/z 14
frag_organic_29 = Org_30*TwentyNine;
frag_nitrate_30 = Thirty - frag_organic_29;
frag_nitrate_46 = FortySix;
frag_nitrate_14 = NO_14_30*frag_nitrate_30 + NO_14_46*frag_nitrate_46;
Ammonia_14 = Fourteen - frag_nitrate_14;
% Ammonia m/z 15
Ammonia_15 = NH_15 * Sixteen;
% Ammonia m/z 16
Ammonia_16 = Sixteen;
% Ammonia m/z 17
frag_water_18 = Eighteen;
Ammonia_17 = Seventeen + (NH_17 * frag_water_18);
%-----------------------------------Nitrate-----------------------------------
% Nitrate m/z 14
Nitrate_14 = NO_14_30*frag_nitrate_30 + NO_14_46*frag_nitrate_46;
% Nitrate m/z 30
Nitrate_30 = Thirty - frag_organic_29;
% Nitrate m/z 31
frag_nitrate_30 = Nitrate_30;
Nitrate_31 = NO_31*frag_nitrate_30;
% Nitrate m/z 32
Nitrate_32 = NO_32*frag_nitrate_30;
% Nitrate m/z 44
Nitrate_44 = NO_44_30*frag_nitrate_30 + NO_44_46*FortySix;
% Nitrate m/z 46
Nitrate_46 = FortySix;
% Nitrate m/z 47
Nitrate_47 = NO_47*frag_nitrate_46;
% Nitrate m/z 48
Nitrate_48 = NO_48*frag_nitrate_46;
   frag_nitrate_48 = Nitrate_48;

%-----------------------------------------Sulfate-----------------------------------------

% Sulfate m/z 48
frag_organic_62 = SixtyTwo;
Sulfate_48 = FortyEight - frag_nitrate_48 - frag_organic_62;
% Sulfate m/z 64
frag_organic_50 = Fifty;
frag_organic_78 = SeventyEight;
frag_organic_64 = Org_64*frag_organic_50 + Org_64*frag_organic_78;
Sulfate_64 = SixtyFour - frag_organic_64;
%
%---------------------------------------------------------------------
% IF Statements
%
% Takes into account negative numbers and the possibility that
% fragments may end up being less than the original count when
% taking into account the contribution from other ions.
%---------------------------------------------------------------------

% IF for Ammonia
if Ammonia_14 < 0;
   Ammonia_14 = 0;
end
if Ammonia_15 > Fifteen;
   Ammonia_15 = Fifteen;
end
if Ammonia_17 < 0;
    Ammonia_17 = 0;
end

% IF for Nitrate
if Nitrate_14 > Fourteen;
    Nitrate_14 = 0;
end
if Nitrate_31 > ThirtyOne;
    Nitrate_31 = 0;
end
if Nitrate_32 > ThirtyTwo;
    Nitrate_32 = 0;
end
if Nitrate_47 > Nitrate_46;
    Nitrate_47 = 0;
end

% IF for Sulfate
% There are no IFs for Sulfate

%-----------------------Organic--------------------------------------
Organic_14 = Fourteen - Ammonia_14 - Nitrate_14;
Organic_15 = Fifteen - Ammonia_15;
Organic_16 = Sixteen - Ammonia_16;
Organic_17 = Seventeen - Ammonia_17;
Organic_30 = frag_organic_29;
Organic_31 = ThirtyOne - Nitrate_31;
Organic_32 = ThirtyTwo - Nitrate_32;
Organic_44 = FortyFour - Nitrate_44;
Organic_46 = FortySix - Nitrate_46;
Organic_47 = FortySeven - Nitrate_47;
Organic_48 = Org_48*SixtyTwo;
Organic_64 = frag_organic_64;

% Sum Organic ions that do not overlap with inorganic ions
i = Final_col1(1:4);
Sum1 = sum(i);
j = Final_col1(9:20);
Sum2 = sum(j);
k = Final_col1(24:34);
Sum3 = sum(k);
Sum4 = FortyFive;
m = Final_col1(40:54);
Sum5 = sum(m);
n = Final_col1(56:441);
Sum6 = sum(n);

% Total Sum of Organic Ions Accounting Overlapping Ions
Sum_Organic = Sum1+Sum2+Sum3+Sum4+Sum5+Sum6+Organic_14+Organic_15...
     Organic_44+...
     Organic_46+Organic_47+Organic_48+Organic_64;

%-----------------------Sum of Inorganic Ions-----------------------

% Sum Ammonia
Sum_Ammonia = Ammonia_14+Ammonia_15+Ammonia_16+Ammonia_17;
% Sum Ammonia
Sum_Nitrate = Nitrate_14+Nitrate_30+Nitrate_31+Nitrate_32+...
     Nitrate_44+Nitrate_46+Nitrate_47+Nitrate_48;
% Sum Ammonia
Sum_Sulfate = Sulfate_48+Sulfate_64;
%-----------------Sum of Inorganic Ions per cm^2-------------------
Sum_Ammonia_cm2 = Sum_Ammonia/Punch;
Sum_Nitrate_cm2 = Sum_Nitrate/Punch;
Sum_Sulfate_cm2 = Sum_Sulfate/Punch;
Sum_Organic_cm2 = Sum_Organic/Punch;

%-------------------Concentration of Species------------------
% Concentration Ammonia
Conc_Ammonia = Sum_Ammonia_cm2/NH_Slope;
% Concentration Nitrate
Conc_Nitrate = Sum_Nitrate_cm2/Nitrate_Slope;
% Concentration Sulfate
Conc_Sulfate = Sum_Sulfate_cm2/Sulfate_Slope;
% Concentration Organic
Conc_Organic = Sum_Organic_cm2/Org_Slope;

%---------------------Headers for Concentrations-------------------
ALL_Centers =
cat(2,Conc_Ammonia,Conc_Nitrate,Conc_Sulfate,Conc_Organic);

cd(Det_Path);

PromptFileName = inputdlg('Save File as...');

xlswrite(input(PromptFileName),ALL_Centers);
## Appendix C

### Three Step Protocol Parameter Table

Table C-1. `cmd3StepProtocol`

<table>
<thead>
<tr>
<th>Secs</th>
<th>Event</th>
<th>Action</th>
<th>Params</th>
<th>Temp</th>
<th>CLV</th>
<th>BVs</th>
<th>FVs</th>
<th>SOF</th>
<th>SPS</th>
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</table>
Appendix D

Comparison between HR-AMS and TOA-QMS organic standards for Elemental Analysis.

Comparison between elemental analyses performed with the TOA-QMS and the HR-AMS. All molecules analyzed with the TOA-QMS were also analyzed with the HR-AMS, but HR-AMS analyzed a few more species.

Figure D-1. O/C determined with TOA-QMS and HR-AMS vs. the nominal ratios of the pure compounds.

Figure D-2. H/C determined with TOA-QMS and HR-AMS vs. the nominal ratios of the pure compounds.

Figure D-3. N/C determined with TOA-QMS and HR-AMS vs. the nominal ratios of the pure compounds.
IGORPRO analysis of O/C, H/C, N/C

Different software packages introduce bias to data analysis. Compared to Microsoft Excel, IGORPRO graphical representation of O/C, H/C, and N/C calibration values are different than values obtained with Microsoft Excel. Figures D4 – D7 show the calibration curve for O/C, H/C, and N/C prepared with IGORPRO. OM/OC remains the same when using the two software packages. See figures 31 - 34 for comparison.

![Figure D-4. O/C EA data plotted with IGORPRO.](image-url)
Figure D-5. H/C EA data plotted with IGORPRO.

Figure D-6. N/C EA data plotted with IGORPRO.

Figure D-7. OM/OC EA data plotted with IGORPRO.
Appendix E

TOA-QMS System Parts

In order to connect the DRI Model 2001 TOA to the mass spectrometer and heat the heated box, the following parts are necessary:

- Agilent Technologies Capillary – Part no 160-2625-10 – Fused Silica, Deactivated – 0.150mm
- Agilent Technologies Ferrule – Part no 5062-3508 – 0.4mm VG cond .25 col
- VICI Valco Instruments Co. Inc. Micrometering valve – Part no. ZBNV1-KZ
- VICI Valco Instruments Co. Inc. – Microvolume Connector – Part no. ZT1
- 2 Omegalux Heat cartridges – Part no. CSS-034100/120

These components are all fitted inside the heated block. Care must be taken when connecting each component. It is advised to first connect the capillary tubing to the mass spectrometer entry port and follow to connect it to the microvolume connector and to the micrometering valve located inside the heated box. Connect the heat box parts to the quartz-glass tube last. Replace the provided stainless steel ferrules with the carbon ferrules from Agilent Technologies. Common leaks are often observed at the quartz-glass tube connection.
References


IPCC, 2013, Climate Change 2013: The physical science basis., Intergovernmental Panel on Climate Change, Cambridge University Press.


Yang, X., Personal communication. 2013.
