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Detecting Organic Molecules on the Surface of Inorganic Dust Particles Using Aerosol Mass Spectrometry

Sileola B. Akinsiku
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DETECTING ORGANIC MOLECULES ON THE SURFACE OF INORGANIC DUST PARTICLES USING AEROSOL MASS SPECTROMETRY

by

Sileola B. Akinsiku

A thesis submitted in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
in
Chemistry

Approved:

__________________________  ___________________________
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Major Professor            Committee Member

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Dr. Robert Brown            Dr. Tom Chang
Committee Member           Committee Member

__________________________  ___________________________
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Committee Member           Dean of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah

2009
ABSTRACT

Detecting Organic Molecules on the Surface of Inorganic Dust Particles Using Aerosol Mass Spectrometry

by

Sileola B. Akinsiku, Master of Science
Utah State University, 2009

Major Professor: Dr. Stephen Bialkowski
Department: Chemistry and Biochemistry

Detection of organic molecules present on the surface of dust particles is important in homeland security, agriculture, and several other applications. The research presented reports the ability of the aerosol mass spectrometer (AMS) to detect molecules on the surface of dust particles without detecting the particle core.

Experiments were carried out to detect semi-volatile organic compounds adsorbed onto the surface of particulates without interference from the dust particle core. Methyl salicylate, oleic acid, and organophosphorus pesticides such as Malathion were detected on the surface of particles representative of dust-type materials. Zeolite powders were used as aerosol support, representative of a typical silica mineral aerosol present in the atmosphere. Mass spectral fingerprint information was gained by first directly detecting atomized species to record their clean electron impact mass spectrum. This facilitated detection during later experiments of organic molecules coated on an inorganic support.
Spectra obtained give mass spectrometric signatures of molecules coated on inorganic particles without detection of the particle core.

An important feature of the AMS is the ability to equate an ion rate detected in the mass spectrometer to a mass concentration of a given chemical species in a sample using its ionization efficiency. Based on an average inlet flow rate of 1.2 cm$^3$ sec$^{-1}$, the ionization efficiencies obtained were 5.89x10$^{-5}$, 1.15x10$^{-6}$, and 1.62x10$^{-5}$ for Malathion, methyl salicylate, and oleic acid, respectively. These experiments and the results obtained show that detection and characterization of organic species adsorbed onto inorganic dust particles are possible at μg m$^{-3}$ concentrations using the AMS.
DEDICATION

My Lord and Savior Jesus Christ, the author of life itself, without whom life would have been an unending search for meaning and the beloved memory of my dad.
ACKNOWLEDGMENTS

I would like to thank Dr. Philip Silva for his help in conducting this research for this thesis, and for his depth of support and understanding throughout my graduate study.

I must also thank my major professor, Dr. Stephen Bialkowski, being your student for one semester gave me new insights into the work been presented, and also my advisory committee members, Dr. Robert Brown, Dr. Tom Chang, and Dr. Randy S. Martin, for their direction, advice during meetings, and impact on my work. And also Dugway Proving Grounds in Utah for funding this project.

My sincere appreciation goes to my mother, Pastor (Mrs.) V. A. Akinsiku, for her care and support in every way possible. You are very special to me, Mom; thank you for all the sleepless nights you have had because of me especially when you came to take care of us during and after Daniel’s arrival; and Mrs. A.O. Ogunlaja for being the best mother any daughter-in-law can pray for.

I am indebted to all my siblings, Mr. & Mrs. S.K. Oni, Mr. & Mrs. Oludayo Fakunle, Oluwabanke Akinsiku, Oludare Mathew-Akinsiku, and Babatomide Omotehinse Akinsiku, for all your support thus far; only God can reward you.

My sincere gratitude goes to all my mentors, Pastor Taiwo Odukoya, Pastor Bimbo Odukoya of blessed memory, Pastor Femi Odumabo, Engr. Frank Eneh, Mr. Bolaji Olawoye for their immeasurable support and for never giving up on me.

During my stay in the United States, a couple of folks have been a part of my family: Tina & Wale Adeleye, Yemisi & Kunle Aladeselu, Brenda & Alvin Suh, Christabel & Eric Tanifum, Tremaine Sterling, Mr. & Mrs. John Obielodan, Mr. & Mrs.
Coe, Lekan, and Stella. Thanks for being more than a friend to me. To all my colleagues in Dr. Silva’s laboratory, I say thank you.

Finally, this piece will not be complete without the two most wonderful people in my life. I will be eternally grateful to the love of my life, Olumuyiwa Omotola Ogunlaja; you are all encompassing, you are indeed my crown, and writing about who you are to me would be a thesis on its own. Thanks for always been there for me. And to my brave angel, Daniel Ireoluwa Ogunlaja, you make my equation complete.

Sileola Bukola Akinsiku
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CHAPTER 1
INTRODUCTION

1.1 ATMOSPHERIC PARTICULATE MATTER

The focus of a wide number of analytical studies has been the identification of harmful organic chemicals in the atmosphere. The majority of matter in the atmosphere is in the gas phase; however, the role of particles is proving to be increasingly important. Particulate matter (PM) is a collective term used for a very small solid particle or liquid droplet found in the atmosphere. PM may be generated by natural processes (e.g., pollen, bacteria, viruses, fungi, mold, yeast, salt spray, soil from erosion) or anthropogenic processes, including diesel trucks, power plants, wood stoves, and industrial processes, and they are subsequently modified by a multitude of processes. Individual particles vary considerably in size, geometry, chemical composition, and physical properties. The effect of particulates on human health and the environment varies with the physical and chemical makeup of the particulates.

One of the major characteristics of PM is particle size. Particles can range in size from 0.005 - 500 micrometers or microns (µm). Sub-micron particles with diameters of less than 1 µm move like gases. Because of their low settling velocities, fine particles may be transported 1,000 kilometers or more from their source. Under the influence of gravity, larger particles do not remain suspended and tend to settle out of the air, sometimes creating localized areas of high particle deposition. The primary category of PM is PM$_{2.5}$; particles with aerodynamic diameter of 2.5µm or smaller. A secondary category of PM is the PM$_{10}$, which includes only particles with aerodynamic diameter of 10µm or
smaller (ten microns is approximately one seventh the diameter of a human hair). Small particles are lodged deeply into the lungs.

Particle size determines the health impacts because different sized particles have different access to the body. The EPA defines particle size using aerodynamic particle diameter, because particles behave with aerodynamic characteristics while in the respiratory system. Particle size will determine how particles behave in the respiratory system. PM that is deposited deep within the respiratory system poses the greatest health risk; typically these are particles from 0.1 to 2.5 micrometers (μm) (Mihelcic, 1999). Exposure to PM can result in a variety of health problems (Dockery et al., 1989; Pope, 1991; U. S. EPA, 2003b; U. S. EPA, 2006b) including irritation of airways, coughing, decreased lung function, aggravated asthma and difficulty breathing, lung-related diseases as evidenced by increased hospitalization, school absences, and lost work days.

Due to the health effects associated with particle size, the EPA has established National Ambient Air Quality Standard (NAAQS) found in the Code of Federal Regulations (CFR) for both PM$_{2.5}$ and PM$_{10}$. The NAAQS for PM$_{2.5}$ is 15 micrograms per cubic meter (μg m$^{-3}$) averaged annually with a 24-hour concentration standard of 35 μg m$^{-3}$ (40 CFR 50.7); and the NAAQS for PM$_{10}$ is 50 μg m$^{-3}$ annually with a 24-hour concentration standard of 150 μg m$^{-3}$ (40 CFR 50.6).

Sources

Particles are either emitted directly into the atmosphere (primary particles) or produced in the atmosphere from the physical and chemical transformation of other vaporous or gaseous pollutants (secondary particles). The major sources of atmospheric particulates are fossil-fuel combustion (which produces ash and soot), industrial
processes (involving metals, fibers, etc.), transportation, wind and soil erosion (producing fugitive dust), and photochemical reactions (complex chain reactions between sunlight and gaseous pollutants). Fugitive dust and particles from industrial processes tend to be larger in size (> 1 µm). Particles from combustion and photochemical reactions are usually smaller in size (< 1 µm). Because of the large number of sources, particulate matter may contain hundreds of different chemical compounds. Fine particles (PM$_{2.5}$) may contain substantial quantities of sulfate, ammonium, nitrate, elemental carbon and condensed organic compounds. Carcinogenic compounds and heavy metals such as arsenic, selenium, cadmium, and zinc are also concentrated in these particles. Larger coarse particles, such as soil particles, fly ash, road aggregate, wood ash, soot, and pollen, are composed primarily of minerals, including silicon, aluminum, potassium, iron, calcium, and other alkaline elements.

1.2 ORGANIC CHEMICALS IN THE ATMOSPHERE

Many individual organic species have been detected in atmospheric aerosols, some of which have very complex chemical compositions. Aerosols may contain refractory components such as black carbon, mineral dust, and sea salt. There are also non-refractory chemical constituents in atmospheric aerosol such as sulfate, nitrate, chloride, and ammonium.

Indeed, low levels of a wide range of mutagenic compounds have been identified in urban particulate matter (Durant et al., 1998). Harmful chemicals can enter the atmospheric aerosol through a variety of pathways. They can be produced as particles, partition into the particulate phase as a result of solubility or semivolatility, or condense on preexisting particles following a conversion or reaction in the atmosphere. For this
reason, a rapid and reliable means of identifying potentially dangerous chemicals on or within particulate matter is highly desirable. One group of harmful chemicals that warrants special attention is pesticides. Human exposure can occur after the application of pesticides to agricultural soils and home-use insecticide and weed sprays (Whitaker and Prather, 2003).

1.3 PESTICIDES

During the twentieth century, growing population has necessitated higher yields in agriculture. To this end, pesticides have become an integral part of modern agriculture. The use of pesticides has increased the yield of crops and has subsequently released hazardous chemicals into the environment. Concerns about the contamination of the atmosphere by pesticides have increased steadily over the last four decades (Majewski and Capel, 1995). A wide variety of pesticides have been observed in the atmosphere rain, snow, and fog (Richards et al., 1987; Glotfelty et al., 1987, 1990a; Brun et al., 1991; Schomburg et al., 1991; Capel, 1991; Nations and Hallberg, 1992; Goolsby et al., 1993; Valsaraj et al., 1993; Franz, 1994; Bester et al., 1995; Majewski and Capel, 1995; Hatfield et al., 1996).

From the 1950s to the 1970s, air was the primary atmospheric matrix sampled and analyzed to assess the atmospheric distribution of pesticides and to quantify volatilization of pesticides and application. Since the 1980s, the studies of pesticides have increased and have been extended to other matrices in the atmosphere to better understand atmospheric processes. Nevertheless, existing literature on the occurrence and distribution of pesticides in the atmosphere is mostly limited to studies that included only
a few pesticides, one matrix sampled, or were short-term or small scale studies (Majewski and Capel, 1995).

Many organochlorine and organophosphorous insecticides have been studied intensively in the atmosphere because of their environmental persistence and toxicity. Even though some of those pesticides have been banned or their use greatly restricted in the United States for decades, they have continued to be detected in the atmosphere at low levels throughout the years (Majewski and Capel, 1995). During the most recent decade, research interest has increased concerning the presence of the current-use pesticides in the atmosphere, especially high-use herbicides. These pesticides have been observed in a number of countries including the United States (Glotfelty et al., 1990b; Goolsby et al., 1993), Canada (Muir et al., 1990; Welch et al., 1991), Switzerland (Buser, 1990), Germany (Scharf et al., 1992; Bester et al., 1995), and Japan (Haraguchi et al., 1995). In the United States, most of these recent studies have been focused in the Midwest due to the high use of these pesticides in this region (Richards et al., 1987; Glotfelty et al., 1990b; Capel, 1991; Nations and Hallberg, 1992; Goolsby et al., 1993; Cromwell and Thurman, 1996). However, there is still less known about the atmospheric processing of the current high-use herbicides and insecticides as compared to the older organochlorine insecticides. More research on a variety of pesticides in the atmosphere is needed to assess the relative importance of local and regional transport of pesticides and the long-term trends of pesticides in the atmosphere.
Uses of Pesticides

Pesticides have played a vital role in the production of food and fiber and in the protection of the human health. The application of agricultural herbicides to control weeds in crop production has increased six-fold between 1965 and 1980 in the United States. Since 1980, herbicide use has remained steady and insecticide use has decreased slightly (Eichers et al., 1968; Gilliom et al., 1985; Aspelin, 1994). The annual total pesticide use, including a wide variety of agricultural and nonagricultural settings, has remained relatively steady at the level of about $5.0 \times 10^8$ kg of active ingredients (AI) of pesticides. Agricultural use of pesticides accounts for 75 percent of total annual use in the U.S. (Aspelin, 1994). Annual use of herbicides accounts for 60 to 70 percent of total pesticides used on U.S. cropland. About two-thirds of herbicide use is for weed control on corn and soybeans. This results in high use of herbicides in the Midwest.

Characteristics of Pesticides

Understanding how pesticides travel in the environment involves a detailed understanding of certain physical and chemical characteristics of pesticides, as well as how these characteristics determine a pesticide's interaction with the environment.

Air Concentration

The concentration of a pesticide (gas or aerosol) in air is the amount contained in a fixed volume of air and is typically expressed as the mass of pesticides per unit volume. Mass is often represented in milligrams (mg) or micrograms (µg) and volume in liters (L) or cubic meters (m³). Pesticides in air may also be measured in terms of mixing ratio with air, often in parts per million (ppm) or (ppb); meaning it occupies one volume for every million or billion volumes of air (Ryan, 1991). Mixing ratios are appropriate to quantify
gases but not aerosols (Hinds, 1999). Described below is the conversion of one concentration measure to another.

\[
1000 \mu g/m^3 = 1 mg/L \\
1000 \text{ ppb} = 1 \text{ ppm} \\
\text{ppm} = \left( \frac{\mu g/m^3 \times (*24.45)}{(**MW)} \right)
\]

where 24.45 is a conversion factor and MW is the molecular weight of pesticides (Dinardi, 1995).

**Solubility**

Solubility is a measure of the ability of a pesticide to dissolve in a solvent, usually water. Pesticides highly soluble in water dissolve easily. Such pesticides are more likely to move with water in surface runoff or to move through the soil in water than are less-soluble pesticides.

Terms such as miscible, dispersible, suspension, emulsifiable, and soluble in water has been used in literature to describe the solubility of pesticides. Also, numerical values such as 2.9 mg/L or ppm have been used to describe the solubility of pesticides. Generally, pesticides with a value of 100 ppm and less are considered relatively insoluble while pesticides with values greater than 1,000 ppm are considered very soluble.

**Adsorption**

Adsorption is the process whereby a pesticide binds to soil particles. Adsorption occurs because of an attraction between the chemical and soil particles. Typically, oil-soluble pesticides are more attracted to clay particles and to organic matter in soil than are water-soluble pesticides. Pesticide molecules with positive charges are more tightly adsorbed to negatively charged soil particles. A pesticide that adsorbs to soil particles is
less likely to move from the spray site than is a chemical that does not adsorb tightly to the soil.

**Persistence**

Persistence is the ability of a pesticide to remain present and active in its original form for an extended period before degrading. A chemical's persistence is described in terms of its half-life, a comparative measure of the time needed for the chemical to degrade. The longer a pesticide's half-life is, the more persistent the pesticide. Persistent pesticide residues are sometimes desirable because they provide long-term pest control and reduce the need for repeated applications. However, some persistent pesticides applied to soil, plants, lumber, and other surfaces or spilled into water or on soil can later harm sensitive plants or animals, including humans. It is especially important to prevent persistent pesticides from moving off-site through improper handling, application, drift, leaching, or runoff. Application of persistent pesticides presents a hazard to persons and non-target animals entering a treated area and may lead to the presence of illegal residues on rotational food or feed crops.

The rate of pesticide degradation relates to the persistence of the pesticide. Degradation processes break down pesticide compounds into simpler and often less-toxic chemicals. Some pesticides break down rapidly – in a matter of days or even hours. Other pesticides can be detected in the environment for a year or more. Pesticides are degraded by the following processes:

1. Chemical degradation is the breakdown of chemicals by processes that do not involve living organisms, most commonly by hydrolysis, a reaction with water.
2. Microbial degradation is the process in which chemicals are degraded by soil microorganisms, such as fungi and bacteria.

3. Photodegradation is the breakdown of chemicals in reaction to sunlight.

Water and temperature both affect the degradation of pesticides. Warm, wet conditions can increase the speed of pesticide degradation; cool, dry conditions slow the degradation process.

**Volutility**

The volatility of a chemical affects the likelihood and levels of a substance existing as a gas in air. Volatility is the tendency of a pesticide to turn into a gas or vapor. Some pesticides are more volatile than others. The likelihood of pesticide volatilization increases as temperatures and wind increase. Volatility is also more likely under conditions of low relative humidity. The potential for a pesticide to volatilize is measured by its vapor pressure. This measurement may be described in units of Pa (Pascal) or mmHg (millimeters of mercury). Pesticides that have high vapor-pressure values are more volatile. Vapors from such pesticides can move off-site and cause injury to susceptible plants or human. Categorization of pesticides based on volatility is described below.
Table 1. Volatility Class of Pesticides (Seiber and Wooddrow, 1984)

<table>
<thead>
<tr>
<th>Class</th>
<th>Vapor Pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile</td>
<td>&gt; $10^{-3}$</td>
</tr>
<tr>
<td>Slightly volatile</td>
<td>$10^{-3} - 10^{-7}$</td>
</tr>
<tr>
<td>Nonvolatile</td>
<td>&lt; $10^{-7}$</td>
</tr>
</tbody>
</table>

**Organophosphorus Pesticides**

Organophosphates (OP) are some of the most widely used pesticides in the world. They are used in agriculture, homes, gardens and veterinary practices, replacing the same uses as the organochlorines, many of which have been banned for years. In general, they are not persistent in the environment as they break down quickly. Because of their relatively fast rate of degradation, they have been a suitable replacement for the more persistent organochlorines.

Organophosphorus pesticides readily undergo biodegradation (unlike the organochlorides, they do not bioaccumulate) and are toxic to a wide range of insects. Unfortunately, some are also toxic to humans due to the similarity to chemical warfare nerve agents. While the OP pesticides cause the same biological effects as nerve agents, there are some important differences in the duration of biological activity and response to therapy. This is due to the phosphorous-sulfur functionality instead of the phosphorous oxygen or phosphorous fluorine function of the chemical warfare nerve agents.

The organophosphates recommended for non-residential uses are relatively toxic to vertebrate organisms. Their primary mode of action on insects and other animals is by phosphorylation of the acetylcholinesterase enzyme. This enzyme is necessary for controlling nerve impulse transmission between nerve fibers. A loss of this enzyme
function results in an accumulation of acetylcholine, which causes unregulated nervous impulses. Higher levels of acetylcholine result in sensory and behavioral disturbances, incoordination and depressed motor function. Symptoms of acute poisoning develop during or after exposure, within minutes to hours, depending on method of contact. Inhalation exposure results in the fastest appearance of symptoms, followed by the gastrointestinal route and then the dermal (skin) route. Some of the early symptoms include headache, nausea, dizziness, sweating, and salivation. Symptoms such as muscle twitching, weakening, vomiting, abdominal cramps and diarrhea all indicate a worsening condition. Recovery from organophosphate exposure depends upon generation of new enzyme. Table 1 shows the mammalian toxicities for organophosphate pesticide.

Malathion is a commonly used organophosphate pesticide on field crops, fruits, nut trees, vegetables, livestock, agricultural premises, and land. The approved uses also include mosquito and medfly control. These uses can result in human skin contact. Malathion has a generally low mammalian toxicity in spite of its strong insecticidal properties. Malathion itself has little or no cholinesterase activity. Like many other organophosphates, Malathion is activated by mono-oxygenase attack to produce the potent anticholinesterase malaoxon. The slow rate of Malathion dermal absorption and its efficient rate of elimination reduces the risk of acute toxicity for all exposures except when involving substantial portions of unprotected skin.
Table 2. Organophosphates Mammalian Toxicities (mg/kg of body weight) (Fishel, 2005)

<table>
<thead>
<tr>
<th>Common name</th>
<th>Rat oral LD&lt;sub&gt;50&lt;/sub&gt;</th>
<th>Rabbit dermal LD&lt;sub&gt;50&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acepate</td>
<td>1.030 – 1.447</td>
<td>&gt;10,250</td>
</tr>
<tr>
<td>Azinphos-methyl</td>
<td>4</td>
<td>150 – 200 (rat)</td>
</tr>
<tr>
<td>Chlorpyrifos</td>
<td>96 – 270</td>
<td>2,000</td>
</tr>
<tr>
<td>Diazinon</td>
<td>1,250</td>
<td>2,020</td>
</tr>
<tr>
<td>Dimethoate</td>
<td>235</td>
<td>400</td>
</tr>
<tr>
<td>Disulfoton</td>
<td>2 - 12</td>
<td>3.6 – 15.9</td>
</tr>
<tr>
<td>Ethoprop</td>
<td>61.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Fenamiphos</td>
<td>10.6 – 24.8</td>
<td>71.5 – 75.7</td>
</tr>
<tr>
<td>Malathion</td>
<td>5,500</td>
<td>&gt;2,000</td>
</tr>
<tr>
<td>Methamidophos</td>
<td>13 (female only)</td>
<td>122</td>
</tr>
<tr>
<td>Methidathion</td>
<td>25 – 44</td>
<td>200</td>
</tr>
<tr>
<td>Methyl parathion</td>
<td>6</td>
<td>45</td>
</tr>
<tr>
<td>Naled</td>
<td>191</td>
<td>360</td>
</tr>
<tr>
<td>Oxydemeton-methyl</td>
<td>50</td>
<td>1,350</td>
</tr>
<tr>
<td>Phorate</td>
<td>2 - 4</td>
<td>20 – 30 (guinea pig)</td>
</tr>
<tr>
<td>Phosmet</td>
<td>147 – 316</td>
<td>&gt;4,640</td>
</tr>
<tr>
<td>Profenofos</td>
<td>358</td>
<td>472</td>
</tr>
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**Environmental Fate of Pesticides**

**Transport in Spray Drift**

The occurrence of pesticides in the atmosphere are due to several processes which include application drift during spraying operations, wind erosion of contaminated soil and post application volatilization (Lee, 1976). Pesticide drift is any airborne movement of pesticides (insecticides, herbicides, fungicides, etc.) away from the intended target, including droplets, dusts, volatilized vapor-phase pesticides, and pesticide-contaminated soil particles. Sometimes drift is very noticeable as a cloud of spray droplets or dust during application, or as an unpleasant odor afterwards. But it can be invisible to the eye
and odorless, persisting for days after application as volatile chemicals evaporate and contaminate the air or adsorbed on particulates. Drifting pesticides can travel for miles, resulting in widespread toxic air pollution. Kegley et al. (2003) showed that in indoor environments, vaporized pesticides can persist for months after an application, concentrating in the air closest to the floor. In addition to human exposure, sensitive aquatic and terrestrial environments may be exposed through atmospheric transport (Majewski ad Capel, 1995). Some instances of elevated levels of toxic pesticide residues in the atmosphere have been reported for agricultural areas in California by Baker et al, (1996). The studies reported so far highlight the concern for pesticide drift following agricultural application.

The best known and most studied of the mechanisms for off-target contamination of food and drinking water is spray drift. The US EPA (1999) has recently defined pesticide drift, concluding that: EPA defines spray drift as the physical movement of a pesticide through air at the time of pesticide application or soon thereafter, to any site other than that intended for application (often referred to as off-target). EPA does not include in its definition the movement of pesticides to off-target sites caused by erosion, migration, volatility or contaminated soil particles that are windblown after application, unless specifically addressed on a pesticide product label with respect to drift control requirements.

This definition clearly refers to spray drift only as what may be termed primary drift, which is the off-site movement of spray droplets before deposition. It does not cover vapor drift, or any other form of secondary drift that may occur after deposition, which is predominantly specific to the active ingredient, whereas spray drift is primarily a
generic phenomenon. The extent that a chemical may drift off-target will depend on a number of variables such as formulation, weather conditions, type of nozzle and droplet size, and in particular, the application method, which can usually be divided into aerial, orchard and ground boom spraying. Of these, the aerial method potentially leads to the greatest drift, particularly if small droplet sizes are used, as is popular in some countries such as Australia. However, it is important to recognize that all methods can lead to drift, particularly if the pesticide is applied poorly, or under adverse conditions.

The main factors leading to drift from aerial application have recently been summarized in the literature as a result of work done by the Spray Drift Task Force in the US (Bird et al., 1996; Spray Drift Task Force, 1997; Hewitt et al., 2002). From an analysis of literature results and experimental work carried out under the Task Force, these papers conclude that droplet size is consistently the primary application variable controlling off-target drift during low-flight applications. Weather, especially wind speed, is also very important, as is spray release position (drift is worse with greater release height and longer spray booms). Bird et al. (1996) recommend that clear specification of nozzles and operating conditions is the best approach for effective management of off-site drift and deposition from aerial applications.

Once released to the environment, chemicals do not generally stay on the target area or initial surface reached. On release, chemicals will tend to partition into air, water, soils, sediments, biota, etc., with the extent of movement into the individual compartments depending critically on their physicochemical properties. This concept is often called fugacity, which can be conceived of as the ‘escaping tendency’ of a substance from any given compartment or phase (Mackay and Paterson, 1981).
Chemicals tend to partition from phases in which they have a high fugacity to those where their fugacity is low. This has led to the generation of a series of models which allow with increasing sophistication the prediction of the global distribution of chemicals, in reality a mass balance of a chemical once released into the environment.

**Transport in Air**

The atmosphere is a very important compartment through which pesticides may be transported in a variety of forms. These include volatilization into the air in the vapour form from plants, water and soils, and transport both in dissolved forms in fog, rain, etc. or adsorbed to particles such as dusts (Majewski and Capel, 1995; Unsworth et al., 1999). Transport may be medium or long-range (inter-regional, intercontinental or throughout the globe). Concentrations of pesticides in air can be expressed per volume of air or in terms of the transport medium if on dust or fog. Transport to the cold, seasonally-low sunlight conditions of the poles may allow substances to become persistent, both because further volatilization is not favored and because they may degrade much more slowly than under the warm conditions in agricultural areas where they were applied (Bidleman, 1999).

**Volatility**

Relatively volatile pesticides may be released directly into air, e.g., methyl bromide (MeBr) during fumigation treatments or Dichlorvos from pest strips. However, pesticides may also move into air indirectly after application. As noted above, many chemicals may move into the atmosphere after the deposition of spray droplets onto the target surface by virtue of their volatility through evaporation or sublimation. Active ingredient properties, meteorological conditions, management practices and the nature of
the soil or crop interact to affect the volatilization rate in the days to weeks over which
volatilization may continue (Bedos et al., 2002). Volatilization of some persistent
pesticides from old residues in soil and water may still be contributing to their transport
in air long after use has ceased in an area (Bidleman, 1999).

Transport on Particles, Including Dust

Movement on dusts or on particulate matter is another pathway for aerial transport
of pesticides, although generally considered to be less important than volatilization
(Majewski and Capel, 1995; Bidleman, 1999). This includes pesticides that enter the
atmosphere adsorbed to eroded dust particles per medium of the wind, or volatilized
chemical that then sorbs onto suspended particulate matter. Far less attention seems to
have been given in the literature to this aspect, although it is suspected that in many
instances measurements of chemicals in air have combined the gaseous and particulate
forms.

Partitioning, Transport and Deposition Processes

Atmospheric contamination of pesticides occurs mainly through their agricultural
use. Most pesticides enter the atmosphere during of shortly after their application,
through spray drift, volatilization from the soil surface, and or wind erosion of soil
particles to which they are adsorbed. The physical chemical properties of the pesticide,
agricultural practices, application methods, and meteorological conditions all influence
the movement of pesticides into the atmosphere (Majewski and Capel, 1995).

Once in the atmosphere, the pesticides are redistributed between the vapor,
particulate, and aqueous phases. The distribution among the phases depends on the air
temperature, presence of liquid water, properties of particles in air, as well as the
physical-chemical properties of pesticides (Tsal and Cohen, 1991). Pesticides that do not undergo transformations and exist predominantly in the vapor phase tend to have longer residence times in the atmosphere. These compounds can undergo long-range transport the atmosphere to areas for from their application sites (Richards et al., 1987; Bidleman, 1988; Kurtz, 1990; Glotfelty et al., 1990b; Goolsby et al., 1993).

Pesticides are removed from the atmosphere by wet and dry deposition, air –water exchange, and chemical reaction. In the wet deposition process, pesticides in the vapor and particulate phases can be washed out by precipitation droplets. This is referred to as the gas or particulate scavenging, respectively. The relative contribution of wet deposition to total deposition depends on the amount and frequency of the precipitation, particle properties and size distributions, particle concentration in air, temperature, and the physical-chemical properties of pesticide (Bidleman, 1988).

Three physical properties of the pesticides: vapor pressure, water solubility, and Henry’s law constant, play important roles in the introduction to, partitioning in, and deposition from the atmosphere. Dynamic processes of dry and wet deposition and gas/particle scavenging are strongly dependent upon the gas/particle partitioning of pesticides in the atmosphere. Therefore, understanding the partitioning of pesticides in the atmosphere is essential to predicting their transport, deposition, and, ultimately their environmental distribution and effects. However, the partitioning between the gas and particulate phases of many of the current high-use pesticides has not yet been studied.

Health Effects

Documented health effects of pesticides include a wide variety of illnesses and diseases, from eye irritation, skin rashes and respiratory problems to neurological
damage, birth defects, cancer and death. The risk for and severity of adverse health
effects from pesticide exposure varies significantly depending on many factors, including
individual characteristics such as age and health status, the specific pesticide, and
exposure circumstances, pesticide concentration, and inhalation rate
(www.epa.gov/ncea/exposfac.htm). Exposure to pesticides at certain developmental
stages of life can result in irreversible damage to organ structure and function. Of
particular concern is the effect of exposure during the reproductive cycle, from
preconception to breast feeding, because of the possibility of poor birth outcomes,
congenital anomalies, developmental deficits, and possibly childhood cancer (Sanborn et
al., 2004). The chemicals used to control pests in agriculture vary widely in their target
organism and mode of action. Due to their low cost, efficacy and wide spread
availability, the largest group of insecticides currently used worldwide is
organophosphates (OPs), which have both agricultural and residential uses (Weiss et al.,
2004). In the United States alone, over 40 million kg of organophosphate pesticides are
applied (Mulchandani et al., 1999). Organophosphates are non-persistent pesticides
(NPP), meaning they break down relatively quickly in the sun, rain and dew found in the
environment and do not accumulate in the body over a long period of time. OPs are
nonetheless a class of neurotoxins harmful to humans and are responsible for tens of
thousands of poisonings in developing countries as reported by (Buckley et al., 2004) and
thousands of poisonings in the US each year (Sudakin et al., 2007). Many OPs are limited
in the extent to which their effects discriminate between target and non-target organisms,
including humans (Costa, 2005).
Organophosphates are highly toxic compounds that act as acetylcholinesterase inhibitors in the peripheral and central nervous system. Their use as pesticides has led to a large number of accidental intoxications in humans and animals. The most toxic of these compounds are the chemical warfare agents (CWA): Sarin (GB), Soman (GD), and VX; for which Malathion vapor is a stimulant and has been fingerprinted. The OP vapours are readily absorbed across the respiratory tract. The absorption rate through the skin of their vapor and liquid forms depends on several factors related to the specific OP (physicochemical characteristics, concentration), the environment (temperature, humidity) and the skin (thickness, density of hair follicles). Following an OP exposure, the efficacy of skin decontamination and treatment can be relatively low if it is delayed. Consequently, respiratory and skin protection are crucial to people potentially exposed to OP (Josse et al., 1999).

OPs have been most extensively investigated for their neurobehavioral toxicity. The first reports of neurobehavioral changes, such as memory impairment, confusion, anxiety, drowsiness, labile emotion, fatigue, depression, irritability in subjects heavily exposed to OP compounds date back to the 1950s and 1960s (Grob et al., 1950; Gerson and Shaw, 1961; Dille and Smith, 1964; Durham et al., 1965; Metcalf and Homes, 1969). Even if these studies were not adequate to reach conclusions, they did, for the first time, underlined the possibility of development of “chronic OP-induced neuropsychiatric disorders” (COPIND). After these early studies, two main lines of study were pursued: the onset of the neurobehavioral impairment as a consequence of an acute OP poisoning and the occurrence of neurobehavioral changes as a consequence of prolonged exposure without preceding episodes of acute poisoning.
As many of the organochlorine pesticides became banned in the 1970s, the agrochemical industry turned to the less persistent, but more acutely toxic, OPs to control insect pests. Nowadays, OPs are the class of agricultural insecticides most widely used in the world. Their extensive use, especially for crop protection, implies an environmental risk, which has risen to an increasing social concern with respect to the presence of OPs in a wide range of surface and ground waters, drinking waters, fruits, vegetables, and foodstuffs in general (Abdel-Halim et al., 2006; Liu et al., 2005; Sun et al., 2006).

Amongst other effects, exposure to high levels of particulate matter coated with these chemicals poses the risk of depositing them into the lungs of humans (Whitaker and Prather, 2003). Thus, detecting organics, particularly OPs on the surface of particulates is an important analytical undertaking.

1.4 THESIS OVERVIEW

The remainder of this thesis will focus on presentation of a study that was designed to detect organic compounds of various vapor pressures adsorbed on the surface of particulates. For these studies we have used an aerosol mass spectrometer. Methyl salicylate, oleic acid and Malathion (an organophosphate pesticide) are the prototype organic species studied. For the studies, dust-type material was chosen as the particulate carrier. Zeolite powder was used as aerosol support, representative of a typical silica mineral aerosol present in the atmosphere. A major goal of the study is the detection and desired quantification of organic species adsorbed on the surface of dust without interference from the particulate core.

Chapter 2 addresses the measurement approach implemented in the aerosol mass spectrometer and some other instrumental and analytical methods that have been used to
detect organic pesticide residues in the atmosphere. Quantification of the AMS data by
ionization efficiency calibration and the technique used in data analysis is detailed.

Chapter 3 details the analysis of laboratory experimental data taken with the AMS
described in Chapter 2 and the materials and experimental setup used in obtaining the
data presented. Results are presented in Chapter 4, followed by a summary of the work
presented and the conclusion.
CHAPTER 2
MEASUREMENT APPROACH USED IN THE AERODYNE AEROSOL MASS SPECTROMETER (AMS)

2.1 REAL-TIME ATMOSPHERIC PARTICULATE MATTER INSTRUMENTATION

Atmospheric PM is chemically complex and labile. Detection and analysis of PM constituents favors real-time instrumental techniques that characterize pertinent physical and chemical properties without having to collect, store, and transport samples. Mass spectrometric (MS) detection techniques for atomic and molecular species are recommended as comprehensive and sensitive in characterizing the chemical content of atmospheric PM. Over the past decade, several research groups have adapted Mass spectrometric methods to meet several challenges. One major theme involves the use of lasers to both vaporize and ionize individual atmospheric particles sample into the mass spectrometer’s source region. This class of instruments focuses on single particle measurements and has been recently reviewed by Noble and Prather (2000) and Sullivan and Prather (2005).

A second class of aerosol mass instruments uses thermal vaporization of individual or collected particles followed by various ionization techniques (Allen and Gould, 1981; Sinha et al., 1982). Of aerosol Mass spectrometric instruments currently available, the most widely used is the thermal vaporization aerosol mass spectrometer (AMS) which was designed and developed at Aerodyne Research, Inc. (ARI) and is currently used by approximately 40 laboratories worldwide. The AMS is described in detail below in Section 2.2.
Existing Instrumentation for Detecting Organic Molecules

Aerosol Time-of-Flight Mass Spectrometry (ATOFMS)

Techniques have been employed to investigate the distribution of pesticides in the atmosphere and their adsorption onto mineral dust particles. One method used was single particle aerosol time-of-flight mass spectrometry (ATOFMS) to detect airborne pesticide residues and chemically classify the dust carrying the pesticide for the purpose of tracking transport mechanisms (Whitaker and Prather, 2003). The method was used to assess the ability of the ATOFMS to identify the presence of these contaminants on individual particles created from pure solutions of several commonly used pesticides, as well as pesticides coated on soils. The method is well suited for the study of trace level pesticides distribution patterns. However the method suffers from the inability to quantify signals.

This instrument is a powerful new tool for providing temporal and spatial information on the origin, reactivity, and fate of atmospheric aerosols. It is capable of analyzing the size and composition of individual particles from a polydisperse aerosol in real-time.

Particles are sampled from ambient atmospheric conditions into the aerosol beam interface depicted in Figure 1. The particles first enter an inlet nozzle at atmospheric pressure and exit at a pressure of 2 torr. This pressure differential causes the gas to undergo a supersonic expansion, during which small particles are accelerated to a higher terminal velocity than large particles. After expansion through the nozzle, the aerosol beam passes through two stages of differential pumping before entering the particle sizing region. The size-dependent velocity distribution within the particle beam is the
basis for determining the aerodynamic diameter of the particles in the particle sizing region of the instrument. Once in the sizing region, the particles pass through a continuous-wave argon ion laser beam, generating a pulse of scattered light which is collected by a photomultiplier tube (PMT). After traveling 6.0 cm, further the particle encounters a second laser beam oriented orthogonally to the first, generating another scatter pulse which is collected using a second PMT. Thus, particle velocity is determined by using the known distance between the scattering lasers and the measured time between the two scatter pulses. Ultimately, upon instrument calibration, this characteristic velocity is used directly to determine each particle’s aerodynamic diameter.

The outputs of both PMTs are sent to a timing circuit, which is used to track the particles and control the firing of the desorption/ionization laser. As the particle is being “tracked”, it continues traveling through the scattering region and ultimately enters the source region of a laser desorption/ionization time-of flight mass spectrometer (LDI-TOFMS).

As the particle reaches the center of the source, the timing circuit fires the desorption/ionization laser. The ATOFMS simultaneously monitors both the positive and negative ions generated by the desorption/ionization event. Calibration of the particle-sizing region was accomplished by nebulizing polystyrene latex spheres (PSL), ranging in size from 0.2 to 7 µm in diameter. The PSLs were suspended in a 50:50 methanol/water solution and nebulized using particle-free air. To ensure that the particles were dry, the output of the nebulizer was sent through a diffusion drier. The particle flow was split and directed into an Aerosizer (API, Model 8050, Hadley, MA) to verify the
Figure 1. Schematic showing the particle beam interface and particle sizing region joined to the mass spectrometer region of the field portable instrument (Gard et al., 1997).

particle size measurement and into the ATOFMS instrument to determine a characteristic particle velocity.

Ion Mobility Spectrometry (IMS)

Another method uses a field portable ion mobility spectrometer (IMS) instrument to detect organophosphorus vapors (Smiths Detection and Draeger) but is unable to carry out direct vapor phase for chemicals with a low vapor pressure.

The term ion mobility spectrometry refers to the method of characterizing chemical substances using gas-phase mobility of ions in weak electric fields. Normally, mobilities are obtained from the time of drift for ions across a fixed length and electric field where time is referenced to the initial injection of ions from the source region to the
drift region (see Fig. 2). Ion mobilities are characteristic of substances and can provide a rapid means for detecting and identifying vapors.

\[
\text{Drift Velocity} : \nu_d = KE
\]

\[
\text{Mobility} : K = \frac{d}{t_d E}
\]

\[
K = \frac{3 \cdot e}{16 \cdot N} \sqrt{\frac{1}{m} + \frac{1}{M} \cdot \frac{\sqrt{2 \pi \left( 1 + \Delta \right)}}{k \cdot T \cdot \pi^2 \cdot \omega}}
\]

where \( E \) is electric field strength, \( d \) is drift path length, \( t_d \) is drift time, \( e \) is unit charge, \( m \) is ion mass (analyte), \( M \) is molecular mass drift gas, \( N \) is number density (drift gas), \( k \) is Boltzmann constant, \( r \) is minimum in the potential curve, \( T \) is temperature, \( \Delta \) is correction term for approximation, and \( \omega \) is collision integral.

As shown in the equations 1 to 3, mobility is related to the electric field strength by the ion drift velocity, which is inversely proportional drift time. Mobility is also related to the collision rate with the gas molecules (reduced mass), the temperature, the dimensions of the ion (structure dependencies), and the collision integral, where the collision integral is influenced by the size of ions or molecules, as well as their structure and polarizability.

Ion mobility spectrometry is selective but depends on several key steps. The first step in the process is ionization. The process of ionization can be made selective for a class of compounds by either physical or chemical processes. IMS ionization is normally achieved by using a \(^{63}\text{Ni}\) radioactive source. The beta radiation electrons from the \(^{63}\text{Ni}\) impact nitrogen in the air and create ions. In air, these ions react by a complicated
mechanism to eventually produce protonated water clusters from atmospheric moisture. The water clusters react with other gas phase molecules to produce positive ions. A reagent gas (pure chemical) is usually added to the ion source to affect selectivity. For example, nerve agents are basic and accept protons easily. Acetone is added to the ion source to eliminate ionization of compounds that are weaker proton acceptors than acetone. The result is that fewer species are ionized and much interference is eliminated. The next step in the IMS process is the migration of the ions in an electric field.

This process separates the ions based on their ionic mobility. Atmospheric pressure electro migration results in broad peaks due to collisions with the gas molecules in the drift region and so the IMS spectra (plasma chromatograms) may be poorly resolved. This problem is exacerbated by a clustering phenomenon noted in the ionization process. Additionally, impurities in the gas (air) that occupies the drift region can add to the reactions and cause irreproducibility. This can be eliminated if purified air is used in the drift region, but this is impractical for field-deployed devices. Separation occurs in the drift tube based on an ionic mobility that has components of mass-to-charge ratio and geometry. The geometry component comes from the collisions that occur between sample molecules and the air. Thus, compounds with the same mass may have significantly different migration times. As a result of these processes, the peak widths seen for laboratory IMS instruments are much better than the field units. As such, IMS detectors for field use are prone to interferences from a variety of sources and exhibit high rates of
false positive and false negative reports. IMS can combine with gas chromatography (GC) for much more reliable detection. The problem is response time. This is an issue whenever traditional chromatography is applied, since the separation of chemicals takes time. However, the most common device used for chemical monitoring by the military is the IMS.

**Gas Chromatography (GC)**

Monitors that employ GC have a sampling interface that traps gases and preconcentrates the sample prior to injection. This process is allowed by the periodic
nature of the analysis and is matched to the required time for the chromatograph to perform the chemical separations process. A balance must be made between the sample processes and the analysis speed. The selectivity of the gas chromatograph is tuned by the choice of stationary phase used in the column. The materials used to coat the capillary are similar to the polymer coatings described for surface acoustic wave sensors (SAWS). Temperature programming of the column is not used in a monitor due to the time required to cool the column for the next injection.

The detector determines the ultimate selectivity of GC. The most selective detectors are spectroscopic, such as Fourier transform infrared (FT-IR) or mass spectrometer. Automated systems can employ chemometrics algorithms to discriminate unresolved chromatographic peaks. These combinations are expensive and require significant computer support. They are more likely to be used in a laboratory for confirmation. Efforts to convert this approach to field units are still ongoing.

Fourier Transform Infrared Spectroscopy (FT-IR)

Spectroscopic methods have higher information content than other methods of detection. The potential exists for the identification of many chemicals. The difficulty in the application of spectroscopic sensing to continuous monitoring is to obtain and process all the information available in a short period of time. This requires a fast scanning instrument combined with a computer that both operates the instrument and identifies the compounds detected. A chemometrics algorithm must deconvolute the spectra because the spectrum will be a composite of several species. The alternative is to find a unique spectral attribute that is indicative of the chemicals of interest. For example, nerve agents have a phosphorus-oxygen double bond (Figure 3) with a characteristic frequency. Nerve
agents can be detected by monitoring this vibrational frequency. There are a couple of problems with this approach. Vibrations in the gas phase have narrow line widths (1.0 cm$^{-1}$ and the IR source width must be matched to include the entire band of interest). The second problem stems from other functional groups overlapping the band necessitating a multiband approach, which means using the complete spectrum. Some very similar compounds are common in the environment, such as organophosphorus insecticides (Figure 4). For example, Dichlorvos, the pesticide used in flea collars, is extremely similar in structure and content to the nerve agents. Consequently, using a gas chromatograph with FT-IR detection is a laboratory option only.

**Mass Spectrometry (MS)**

Mass spectrometry has long been used for the detection of low molecular weight gases. The devices are called residual gas analyzers and are typically magnetic sector or quadrupole instruments. The quadrupole mass spectrometer is usually the analyzer of choice for gas analysis since it can tolerate higher pressures than other analyzers. The primary use for these devices is to detect molecules that survive electron impact ionization without extensive fragmentation.

This approach can be applied to chemical agent detection with the addition of detection algorithms designed to recognize the fragmentation pattern of the agents. However, it is difficult to interpret spectra from a combination of compounds without prior separation. Mass spectrometers can scan rapidly, so that fast GC methods are applicable. Tandem mass spectrometry (MS-MS) uses one mass spectrometer to select a specific ion from a sample to be further fragmented and mass analyzed by a second mass
Figure 3. Chemical structure of nerve agents a) Sarin, b) Soman, c) Tubun, and d) VX.

Figure 4. Chemical structures of two common insecticides: a) Diclorvos and, b) Phosdrin.

spectrometer. This method could have a speed advantage but is difficult to implement when a variety of chemicals need to be detected.

Furthermore, a number of analytical methods have also been employed for the characterization and identification of specific organic compounds adsorbed onto collected mineral dust particles. Some of these techniques are as follows: Falkovich and Rudich (2001) and Mamane et al. (1980) proposed SEM-EDS (Scanning electron microscopy equipped with energy dispersive system), used for surveying the adsorption of organic compounds onto individual particles, direct sample introduction gas chromatograph/mass spectrometry (DSI/GC/MS), and ion chromatography (IC) were presented by (Falkovich and Rudich, 2001) for identifying specific organic tracers in bulk samples.
2.2 THE AEROSOL MASS SPECTROMETER

Overview

The Aerodyne quadrupole aerosol mass spectrometer (Q-AMS) was designed to measure size-resolved mass distributions and mass loadings of volatile and semi volatile chemical species in/on submicron particles (Jayne and Leard, 2000). It is capable of near real-time detection and quantification of size-resolved mass concentrations of aerosol-phase species with a time resolution of minutes. Unlike laser-desorption/ ionization instruments that provide a qualitative or semi-quantitative picture of the full chemical composition of individual particles, the AMS provides quantitative composition information on ensembles of particles, with limited single particle information (Suess and Prather, 1999). The instrument has been described in detail previously by Jayne and Leard (2000) and Allan et al. (2003) but a description of the instrument as used in the work presented in this thesis is given here.

The AMS, shown in Figure 5 and 6, draws particles into vacuum through an aerodynamic lens sampling inlet system (Liu et al., 1995a; Liu et al., 1995b; Zhang and Smith, 2002) The lens focuses aerosol particles into a narrow, collimated beam that impacts on a porous tungsten surface (the vaporizer) heated typically to 600°C under high vacuum (~ 10^{-8} torr). The non-refractory fraction of the particles, mostly the volatile and semi-volatile components, flash vaporize upon contact with the vaporizer surface on a time scale of a few microseconds, and the resultant gaseous molecular constituents are ionized using a 70 eV electron impact (EI) source positioned such that the maximum electron density and the center of the vaporized plume are co-located in the extraction zone of the mass spectrometer. A quadrupole mass spectrometer (QMA 410, Balzers
Instruments, Balzers, Liechtenstein) is utilized to analyze the positive ions with unit mass-to-charge ($m/z$) resolution. This chapter describes the individual components of the AMS, its principles, modes of operation, and how it can provide quantitative measurements of the chemical composition and size distribution of submicron aerosol particles.

Figure 5 shows layout picture of the instrument. Ambient air is sampled through a critical orifice into an aerodynamic lens, which focuses particles ranging from about 35 nm to 1.5 µm in size into a narrow beam (Allen and Raabe, 1982). Orifice diameters 100 and 120 µm have been used, which give nominal inlet flow rates of about 1.5 and 2.0 cm$^3$ s$^{-1}$ at standard temperature and pressure (STP), respectively.

The AMS consists of three main sections: (1) a particle generation chamber, (2) an aerodynamic sizing chamber, and (3) a particle composition chamber. Each chamber is differentially pumped, reducing the sampled gas flow from the lens such that the particle mass is concentrated by a factor of $10^7$ compared to the ambient air. With the exception of the major components of air (N$_2$, O$_2$, Ar, H$_2$O, and CO$_2$), there is no detectable interference of vapor components in the measured particulate mass spectrum.

The aerosol sampling chamber couples the aerodynamic particle beam-forming lens to the vacuum system (Lui et al., 1995a). The lens focuses particles into a narrow beam with nearly 100% particle transmission efficiency to the detector for particles in the size range between 70 and 600 nm in diameter (Zhang and Smith, 2002). Ambient pressure particle-laden air is pumped through this lens into the vacuum region of the mass spectrometer which accelerates them to a velocity proportional to their size.
Figure 5. A picture of the Aerodyne aerosol mass spectrometer (AMS).

Particles that have been sampled by the AMS impact on a vaporizer composed of a tungsten surface that heats volatile and semi-volatile components into gaseous species. These gas-phased species are ionized using conventional electron-impact (EI) ionization as shown in Figure 7.

The resulting positive ions are introduced into a quadrupole mass spectrometer for filtering according to mass to charge ratio before being detected by an electron multiplier. The signal from the multiplier is fed through a preamplifier to a data acquisition system (National Instruments, Austin, TX, USA) in the logging computer. For this experiment, the vaporizer operated at various temperatures from ~200°C – 900°C and ionization was performed using 70eV electron impaction.
Modes of operation

The Q-AMS can be operated in two different modes. In the first mode, the ‘‘mass spec’’ (MS) mode, the quadrupole mass spectrometer is operated in a scanning manner. For this experiment, the analyzer was scanned from 0 to 300 mass-to-charge ($m/z$) to provide mass spectral data on the ensemble particle sample. In this mode, quantitative mass loading information on particulate ammonium nitrate, sulfate, and carbonaceous material can be obtained as has been described by (Allan et al., 2003). The logging and control software records the multiplier signal as a function of $m/z$, generating mass spectra. A mass spectrum of the particle and gas beam is obtained by subtracting the average mass spectrum acquired when the chopper is in the blocked position from the average when the chopper is in the open position.
This removes any contribution from background gas in the detector (the operating pressure in the detection region is <10\(^{-7}\) torr). As this background varies with time, it is important to measure this continuously. In addition to providing qualitative information on the composition of the aerosol ensemble, quantitative ambient mass concentrations (in \(\mu g \, m^{-3}\)) for chemical species can be derived from the mass spectra. Summarily, empirically determined ionization efficiencies for chemical species detected by the Q-AMS are used to convert ion counts (in Hz) into quantitative mass loadings. Sensitivity drift of the mass spectrometer during an experiment can be directly measured by monitoring the signal from the gas-phase nitrogen “airbeam.”

The second mode of operation of the AMS is the ‘‘time-of-flight’’ (TOF) mode. This mode of operation is based on the fact that aerosol particles gain a velocity distribution as they accelerate from the aerodynamic lens into vacuum. The final velocity is dependent on particle size, shape and density. The quadrupole mass spectrometer is set to detect one mass fragment (\(m/z\)) over several chopper cycles but is programmed to
cycle through several selected mass-to-charge ($m/z$) settings at a 3 Hz rate. The settings for $m/z$ typically are chosen so that they can be identified with specific chemical species. At the same time, the particle beam chopper is positioned in a way that allows pulses of aerosol particles and gas phase material through at regular intervals. As the disc of the chopper rotates, aerosol particles can only pass through when one of the chopper disc slits is in line with the particle beam. The chopper spins at a frequency of 100 to 150 Hz, allowing for a time-of-flight cycle of 10 ms or less. The time taken by a particle to travel from the chopper assembly until it is detected by the quadrupole mass spectrometer can be used to calculate its velocity, giving the known distance between them. This method assumes that the time taken for ions to reach from the ionization cell to the electron multiplier detector is negligible and has been shown to be the case for non-refractory aerosol (Jayne and Leard, 2000).

2.3 THEORY OF AMS QUANTITATIVE MEASUREMENTS

The ability to equate the detected ion rate in the mass spectrometer to a mass concentration of a certain chemical species in the sampled aerosol particles is a very important feature of the AMS (Canagaratna et al., 2007). The data acquisition software receives the voltage outputs from the preamplifier, which are directly proportional to the electrical current outputs of the electron multiplier detector. The latter are divided by the average single ion signal strength in order to be converted to detected ion rates. The following formula was adapted by Jimenez et al. (2003) from Bley (1988) in order to convert an ion rate signal, $I$, to the equivalent mass concentration, $C$ in $\mu$g m$^{-3}$:

$$C = \frac{10^4 MW}{IE Q N_A} I$$

(4)
where $MW$ is the molecular weight of the parent species, $N_A$ is Avogadro’s number, $Q$ is the volumetric flow rate into the AMS, and $IE$ is the ionization efficiency. It is important to note that the $IE$ depends both on the ionization efficiency for producing charged ions and the transmission efficiency of the quadrupole mass spectrometer of those ions.

During electron impact ionization, molecules of most chemical species undergo fragmentation which results in various numbers of mass fragments ($m/z$) depending on the structure of the chemical species under study. For example, the nitrate group (NO$_3^-$) produces two major mass fragments in the mass spectrum of ammonium nitrate at $m/z$ 30 and 46 arising from NO$^+$ and NO$_2^+$, respectively. To measure the total mass of nitrate, the formula above must be updated to account for both fragments as follow:

$$C_{NO_3} = \frac{1}{IE_{NO_3}} \frac{1}{Q} \frac{MW_{NO_3}}{N_A} \sum_{j=30,46} I_f$$

The ionization efficiency of nitrate, $IE_{NO_3}$ is measured during routine calibration, as described by (Jayne and Leard, 2000) and discussed in Section 2.3. The following correction, which is independent of chemical species, should be applied to all AMS data to account for varying instrument response for different $m/z$ values.

$$I_{m/z}^{corrected} = \frac{I_{m/z}^{measured}}{T_{m/z} \cdot G_{m/z}}$$

where $I_{m/z}^{corrected}$ is the signal intensity as a function of $m/z$, $T_{m/z}$ is the relative transmission of the quadrupole mass spectrometer for a given $m/z$ and $G_{m/z}$ is the relative gain and detection efficiency of the electron multiplier. The relative transmission of the quadrupole as a function of $m/z$ has not yet been determined, though should be a minor correction according to the manufacturer (Balzers Instruments, 2000).
This method can be extended to calculate the mass concentration of other chemical species such as sulfate, ammonium, or carbon by summing the signals of the appropriate mass fragments \((m/z)\) and relating the \(MW_s/IE_s\) ratio of this species to a measured \(MW/IE\) ratio of a calibration compound such as ammonium nitrate (\(\text{NH}_4\text{NO}_3\)).

The assumption is that the ionization cross section of the parent molecules is proportional to the number of electrons present. Jimenez et al. (2003) used the NIST data for electron impact ionization cross sections \((\sigma)\) with 70 eV electrons versus the number of electrons in the molecule (Figure 8) to illustrate the validity and limitations of this assumption. The ionization efficiency of a molecule is directly proportional to \(\sigma\) since the latter represents the efficiency of ionization of a per-molecule basis. The number of electrons in a molecule, \(N_e\), is highly correlated with its molecular weight due to the fact that the ratio of atomic number to atomic weight is very similar for most of the atoms of the molecules found in atmospheric aerosol particles such as C, O, N and S. This leads to the assumption that since \(IE_s\) are directly proportional to \(\sigma\), and \(N_e\) is approximately proportional to \(MW_s\), that \(IE_s/MW_s\) will be proportional to \(\sigma/N_e\). It can be inferred from Figure 8 that \(IE_s/MW_s\) is approximately constant for molecules of a given type, allowing for the following generalization to be made about a chemical species \(s\), when compared to nitrate:

\[
\frac{MW_s}{IE_s} = \frac{1}{K_e} \cdot \frac{MW_{\text{NO}_3}}{IE_{\text{NO}_3}}
\]  

(7)

where \(K_e\) is a dimensionless constant, specific to the chemical species type and can be determined experimentally. It has been found that \(K_e\) is equal to 1 for most inorganic
species, approximately 2 for hydrocarbons, and 1.5 for oxidized organic compounds (P.J. Silva, Aerodyne Research, Inc., unpublished laboratory data, 2002).

A generalized formula for the calculation of the mass concentration, in $\mu g \; m^{-3}$, for a particular chemical species, $s$, can be obtained by incorporating equations 6 and 7 into 5, as follow:

$$C_s = \frac{R_t \sum_{i} I_{i}^{corr} \cdot MW_{NO_3}}{N_A Q \cdot IE_{NO_3}}$$  \hspace{1cm} (8)

where $\sum_{i} I_{i}^{corr}$ is the total ion current (ions s\(^{-1}\)) for all the mass fragments produced by a given species (s), $MW_{NO_3}$ is the molecular weight of nitrate (62 g mol\(^{-1}\)), $IE_{NO_3}$ is the measured ionization efficiency for nitrate, $N_A$ is Avogadro’s number and $Q$ is the volumetric flow rate into the AMS.

Figure 8. Electron impact ionization cross section as a function of the number of electrons in a molecule for various inorganic and organic compounds (Jimenez et al., 2003).
$R_z$ is a response factor that takes into account the differences in ionization efficiency per unit mass for different species with respect to the measured $MW_{NO_2}/IE_{NO_2}$ is the inverse of the relative ionization efficiency per unit mass for species $s$, $RIEs$. In practice, the measured $IE_{NO_2}$ is determined only from the ion fragments 30 (NO$^+$) and 46 (NO$_2^+$) during calibration. Laboratory work has shown that these signals account for about 90% of the total nitrate ion signal for ammonium nitrate (Hogrefe et al., 2004). Thus, $RIEs$ also accounts for this difference between the true $IE_{NO_2}$ and the measured $IE_{NO_2}$.

Equation 8 requires that the ion signals produced by a given species at all $m/z$ peaks are known. In some experiments, however, the contribution of a species to certain peaks in the mass spectrum cannot be directly measured due to overwhelming interference from other ions detected at the same $m/z$, such as the S$^+$ peak ($m/z$ 32) in the sulfate spectrum, which is dwarfed by the O$_2^+$ peak from gas phase oxygen when sampling in air. The AMS data analysis software package described by Allan et al. (2003, 2004), and briefly described in Section 3.6 of this manuscript, attempts to account for the non-measurable $m/z$ peaks for each species by using ratios derived from laboratory calibrations to estimate the peaks that cannot be measured (such as $m/z$ 32 arising from the vaporization/ionization of sulfate). Equation 8 can be rewritten as:

$$C_s = R_z C_s^{eq}$$  \hspace{1cm} (9)

where $C_s^{eq}$ is known as the nitrate-equivalent mass concentration of a given species ($s$), i.e. the mass of nitrate that would produce an ion current equivalent to that detected for the species (Jimenez et al., 2003).

However, it has been observed that the direct application of equations 8 and 9 underestimates the aerosol sulfate mass concentrations when comparing AMS data to
data from other collocated instruments by a factor of 2 (Drewnick et al., 2003). Based on several additional laboratory and field tests (Allan et al., 2004) it is believed that a significant fraction of the observed underestimation is due to the fact that some ambient particles are irregular in shape and a fraction of them do not reach the vaporizer due to either the known lower focusing efficiency of the aerodynamic lens inlet for nonspherical particles (Liu et al., 1995b; Jayne and Leard, 2000; Kane and Johnston, 2000) or to particle bounce on the vaporizer surface. To characterize these effects, the particle collection efficiency, $CE_s$, has been defined as the fraction of the sampled particle mass of a given species that reaches the AMS detector (Alfarra et al., 2004). From a physical point of view, $CE_s$ should actually be defined for particles and not species, and in principle could be a function of particle size for particles of the same composition and physical shape. To take into account this effect, equation 9 is re-written as:

$$C_s = R'_t C_s^{eq}$$

(10)

where the only change is the replacement of $R_z$ by $R'_z$ in order to include the particle collection efficiency, $CE_s$. $R'_z$ is then defined as:

$$R'_t = \frac{1}{RIEs \cdot CE_s} = R_t \frac{1}{CE_s}$$

(11)

The values of the relative ionization efficiencies for different species, RIEs, are obtained from laboratory calibrations of pure species, while the collection efficiencies of different species are inferred from comparisons of AMS data to external measurement techniques.
2.4 AMS OPTIMIZATION

There is an extensive set of calibrations that has to be carried out to ensure that the AMS is operating at optimum performance and producing quantitative results. The IE calibration is one important one.

Ionization Efficiency Calibration

Ionization efficiency (IE) can be defined as the ratio of the number of ions produced to the total number of available parent molecules for that ion species (e.g. if the ionization efficiency is 1x 10^{-6}, then 1 molecule in 1 million molecules is ionized). For any given parent molecule, the total number of ions produced can be calculated by a sum of the ion intensities of all its fragment ions. The number of available parent molecules can be determined from the product of the number of moles and Avogadro’s number. This can be easily calculated for particles of known size and composition, where density and molecular weight are known.

The ionization efficiency calibration is also known as the mass or nitrate calibration. The purpose of this calibration is to calculate the ionization efficiency (IE) of a material that has a known molecular weight (MW). Ammonium nitrate (NH₄NO₃) has been chosen as a primary calibration material because of its volatility, which enables near 100% particle vaporization and does not leave much residue to interfere with subsequent measurements. In addition, ammonium nitrate particles can easily be generated from aqueous solutions and the material is readily available at a reasonable cost.

During a typical AMS calibration, the ionization efficiency of nitrate (IE_{NO₃}) is calculated using Equation 4 by determining the number of ions produced per particle of
350 nm NH$_4$NO$_3$ particles, generated from an aqueous solution and size selected by a Differential Mobility Analyzer (DMA) discussed subsequently in Chapter 3.

\[ IE_{NO_3} = \frac{\text{IP} \times \frac{d_m}{\rho} \times \frac{1}{1} \times e^{-21} \times \chi_v \times f_{NO_3}}{N_A} \times \frac{MW_{NO_2}}{N_A} \]  

(12)

where $\text{IP}$ is “Ions produced per particle” determined during the calibration by dividing the sum of all nitrate ions by the total number of detected particles, $d_m$ is the mobility diameter of the DMA size selected particles (350 nm), $\rho$ is the density of the NH$_4$NO$_3$ particles (1.72 g/cm$^3$), and $\chi_v$ is a shape factor (0.8), $f_{NO_3}$ is the fraction of NO$_3$ in NH$_4$NO$_3$ (0.775) and $N_A$ is Avogadro’s number.

The majority of aerosol particles selected by a DMA will be singly charged and have the desired diameter, however a small percentage of particles will be considerably larger than the desired diameter, but still be selected by DMA as discussed in Chapter 3. This happens because the charge distribution on the aerosol entering the DMA approximately follows Boltzmann statistics after passing through the neutralizer. This gives rise to multiple charging phenomenon; where larger particles with two charges or more appear to have the same mobility diameter as the singly charged desired particles. However, these particles can be size resolved by the AMS as multiple peaks in the TOF mode of operation, and only particles arriving at the time that corresponds to the singly charged particles are selected for calibration.

The $IE_{NO_3}$ calibration is highly influenced by any changes made to the ionizer setup or the quadrupole mass spectrometer. The procedure should be performed following any tuning of the quadrupole mass spectrometer voltages to ensure accurate
quantitative results. This calibration should also be carried out at the start of each experiment and needs to be checked every few days of operation.

2.5 DATA ANALYSIS TECHNIQUES

A suite of analysis tools that can be used for producing quantitative AMS results have been developed at University of Manchester Institute of Science and Technology; UMIST (Allan et al., 2003, 2004). The analysis program has been developed using IGOR PRO; a software package that has its own programming language, supplied by wavemetrics (http://www.wavemetrics.com) The analysis tools have been designed so they can be applied to any AMS dataset and they are currently in use by most groups within the AMS users community. After loading the AMS raw data from both MS and TOF modes of operation, a number of user-defined corrections can be applied to either or both of them.
CHAPTER 3

INVESTIGATIONS INTO USING THE AMS TO DETECT ORGANIC MOLECULES ADSORBED ONTO INORGANIC PARTICLES

3.1 EXPERIMENTAL SET-UP

A Wright dust feeder (Allen and Raabe, 1982) was used to mobilize Zeolite dust. Zeolite dust was used for this project due to its unique characteristic features. Zeolites are microporous crystalline solids with well-defined structures. They have pores with molecular dimensions that leads to their shape selectivity. There is a narrow range of pores sizes in the solid because the materials are crystalline, giving it a better selectivity than non-crystalline materials. Generally they contain silicon, aluminum and oxygen in their framework and cations, water and/or other molecules within their pores. Many occur naturally as minerals and are extensively mined in many parts of the world. Others are synthetic and are made commercially for specific uses or produced by research scientists trying to understand more about their chemistry.

The properties of zeolites including acidity, ion interchange and molecular sieving enables them to be used in a large variety of industrial and research applications, such as gas separation, adsorption, catalytic cracking, catalytic reforming and fine chemicals synthesis and many others (Mora-Fonz, 2005). In a similar way, zeolites can absorb ions and molecules and thus act as a filter for odor control, toxin removal and as a chemical sieve. Zeolites can have the water in their structures driven off by heat with the basic structure left intact.

The Wright dust feeder, Figure 9, is a standard tool in aerosol science used to generate super micron inorganic particles. Details of its design and construction have been described by Wright (1950); only a brief description is given herein.
The Wright dust feeder consists of a cylindrical reservoir, a hollow stem, and a wiper arm that rotates to scrape the surface of the powder in the reservoir in which dust is packed into a cake. The dust is compacted in the reservoir and the scraper separates a thin film of dust into an air stream at the surface. A schematic diagram of the feeder is shown in Figure 10. The instrument comes with a large (A) and small dust reservoir. There is a corresponding large (K) and small scraper head. To commence experiments the scraper of choice is fitted to the reservoir and long pinion (C) is pulled so as to disengage pinion (E) from gear (D). Cup (A) is unscrewed from Cap (B) along with the scraper head (K). It has been found that any dust which is clean and dry with most particles below 10 micrometers diameter, can be packed in this way, and will form a stable cake; yet when the dust is scraped off the surface, it can be readily dispersed. A controlled pressure drop is applied between the inlet, H and outlet, D of the feeder, driving a gas flow across the surface of the powder in the reservoir where it entrains the separated powder into the
reference flow. The mass loading of powder in the reference gas can in principle be varied by varying the pressure drop across the feeder. A variable speed motor provides adequate power for driving the mechanism over a revolution range of about 1000:1. By this, an extremely thin layer of dust is scraped off at each revolution of the holder (0.007") or 0.18mm. A large dust chamber with an internal diameter of 1.5 inches (38mm) was used which was sufficient for the desired concentration of less than ~10 mg/liter without producing aggregation of particles. It produced a uniform distribution of the 4 Å pore sized particles used for the experiment.

Also for this study, we generated mono dispersed, submicron sized inorganic solid phase support particles using a constant output Collision atomizer (BGI Inc.) coupled with a diffusion dryer. A differential mobility analyzer (TSI, DMA 3071) was used to select atomized particles that fall within a narrow range of electrical mobility.

Figure 10. Schematic diagram of the historical Wright dust feeder from original publication (Wright, 1950).
from a steady stream of charged particles suspended in a gas. The DMA, sometimes known as an electrostatic classifier (Knutson and Whitby, 1975; Flagan, 1998) is a useful tool for generating monodispersed (i.e. containing only one size of particle) aerosols. The sizes of particles in this range are ~ 300-700 nm. The narrow range of electrical mobility in the aerosol that is classified by the DMA directly translates to a narrow range of particle size. Size range is constrained on the range of voltages that can be scanned.

As an example, Figure 11 shows the DMA design introduced by (Winklmayr et al., 1991) also known as the Vienna design, although other versions exist (Flagan, 2004).

The device consists of a hollow, earthed cylinder with a concentric rod in the centre, to which a positive voltage is applied. Before entering the DMA, the polydisperse (containing more than one size of particle) aerosol sample flow is passed through a neutralizer (e.g. TSI model 3077), which ensures a predictable distribution of charge.

![Figure 11. A schematic of a ‘Vienna design’ differential mobility analyzer (Winklmayr et al., 1991).](image-url)
A neutralizer normally works by flowing the aerosol past a radioactive source, such as $^{85}$Kr or $^{210}$Po; Po was used in this project, which charges the gas molecules present in the aerosol. Particles with positive or negative charges are neutralized by successive collisions with the oppositely charged gas molecules. When equilibrium is reached, most particles are neutrally charged, while a fraction will have a small positive or negative charge of one or more elementary charges ($e$). The polydisperse aerosol flow is introduced at the outer edge of the DMA cavity, while particle-free air (known as the sheath gas) is laminarly flowed past the central rod at a volumetric rate of approximately 10 times that of the polydisperse flow. As the combined flow passes up the length of the cylinder, particles with negative charges in the polydisperse flow will migrate through the sheath gas towards the central rod at speeds where the electrostatic force they experience is balanced by their drag forces. The particles that reach the central rod at a particular point are drawn through a slit.

The speed of a particle in a given electric field, or electromobility, is dependent on its electrostatic charge, its size and its geometry, as well as the properties of the sheath gas it is moving through. A particle’s electromobility diameter, or $D_m$, is defined as the diameter of a sphere with a charge of $-e$ that would have the same electromobility under the same conditions.

Note that unlike the aerodynamic diameter, this is completely independent of the particle’s density. Also note that for a given $D_v$, an increase in a particle’s irregularity (thereby increasing its drag) will increase its $D_m$ but decrease its $D_a$ and $D_s$. It is important to remember these differences when comparing data from separate instruments.
The experimental set-up in Figure 12 shows how the zeolite powder is entrained in an airflow using a Wright dust feeder. The outlet of the Wright dust feeder is connected to a round bottom, three neck, and outer joint flask. One neck serves as the inlet for the dust, the second neck is used as a thermometer hook-up for monitoring the temperature of the vapor, and the third neck is the outlet to the AMS. The round bottom flask is heated using a heating mantle for provision of direct, even heat to a large surface area creating an excellent heat distribution without spattering.

The schematic diagram for this study is as shown in Figure 13. It shows the process flow for the two major experimental data type obtained. The first route is the set-up used to obtain the atomized spectrum described previously; atomized organic solutions generated in the collision atomizer is passed through a diffusion dryer, then into a DMA and finally to the AMS for analysis.
The second route is through the Wright dust feeder which generates dusts, which are then mobilized at a selected speed into a 3-neck round bottom flask where it is coated with organic vapors and finally into the AMS for analysis.

![Schematic diagram of experimentation set-up.](image)

3.2 MATERIALS USED

Zeolite powder (Molecular sieves, 4A, powder, < 5 μm, Sigma-Aldrich) was used as inorganic solid support. Methyl salicylate (Sigma-Aldrich), Oleic acid (Fisher/Acors) and Malathion mixture (~40% Malathion, ~50% aromatic solvent (mostly xylene derivatives), and ~10% emulsifier (exact composition unknown)) were chosen as the prototype organics. Selected properties of some of these substances are presented in Tables 3, 4 and 5. The Malathion mixture was purified by first separating the aromatic
components by volatilization. The remaining malathion/emulsifier sample was used to coat dust particles using heat to convert malathion into vapor. Since the emulsifier is non-volatile, only the malathion coated the zeolites.

Table 3. Selected Physicochemical Properties of Malathion

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>$\text{C}<em>{10}\text{H}</em>{19}\text{O}<em>{6}\text{PS}</em>{2}$</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>330.36 g mol$^{-1}$</td>
</tr>
<tr>
<td>Water solubility at 20°C</td>
<td>$1.43 \times 10^2$ mg L$^{-1}$</td>
</tr>
<tr>
<td>Melting point</td>
<td>2.85 °C</td>
</tr>
<tr>
<td>Vapor pressure at 25°C</td>
<td>$7.90 \times 10^{-6}$ mm Hg</td>
</tr>
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</table>
Table 4. Selected Physicochemical Properties of Methyl Salicylate

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<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>$C_8H_8O_3$</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>152.15 g mol$^{-1}$</td>
</tr>
<tr>
<td>Water solubility at 30°C</td>
<td>$7.00 \times 10^2$ mg L$^{-1}$</td>
</tr>
<tr>
<td>Melting point</td>
<td>-8°C</td>
</tr>
<tr>
<td>Vapor pressure at 25°C</td>
<td>$3.43 \times 10^{-2}$ mm Hg</td>
</tr>
</tbody>
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Table 5. Selected Physicochemical Properties of Oleic Acid

<table>
<thead>
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<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>$C_{18}H_{34}O_2$</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>282.47 g mol$^{-1}$</td>
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<tr>
<td>Water solubility at 25°C</td>
<td>$1.15 \times 10^2$ mg L$^{-1}$</td>
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<tr>
<td>Melting point</td>
<td>13.4°C</td>
</tr>
<tr>
<td>Vapor pressure at 25°C</td>
<td>$5.46 \times 10^{-7}$ mm Hg</td>
</tr>
</tbody>
</table>
CHAPTER 4
RESULTS AND DISCUSSION

Oleic acid, methyl salicylate (MES), and Malathion were chosen as prototype organic simulants. Malathion is a model low volatility wide-spectrum neurotoxin and a member of the organophosphate class of chemicals receiving attention because of its harm to humans, livestock and wildlife. Our work first involved the use of Q-AMS to directly detect generated atomized species with no coating on dust. This allowed us to verify the ion peaks (already known from NIST database) characteristic of these organic compounds and also aide our later interpretation of mass spectra of organic compounds coated on inorganic support particles.

4.1 AMS MASS SPECTRUM OF ATOMIZED METHYL SALICYLATE AND MALATHION

The organic molecules were atomized to give a pure particle for ionization efficiency calculations. The particles were dried using a diffusion drier and passed through a DMA used to size classify the particle stream to give a mono-dispersed particle distribution. Mass spectra of both compounds were obtained using the AMS.

The background and air-subtracted mass spectrum of atomized methyl salicylate is shown in Figure 14. The largest \( m/z \) fragment ion observed was 18; this is probably due to thermal decomposition of the hydroxyl group into water. Because of the elevated vaporizer temperature of the AMS, fragment ions due to thermal decomposition are often observed in the EI mass spectra. The peaks in black show that on a relative abundance basis, \( m/z \) 17 and 18 (fragments from \( \text{H}_2\text{O}^+ \)) dominate the spectrum of MES detected using the AMS. The spectrum in gray excludes all \( m/z \) ratios below 20 as is more typical
of EI MS database searches. When looking only at the higher mass ions, the base peak becomes $m/z$ 120. Other major ions detected include the parent ion (152) and fragment ions $m/z$ 92, 65, 44, and 29. The presence of $m/z$ 44 as a major component also indicates some thermal decomposition of MES on the vaporizer. It probably results from CO$_2$ emitted from the carboxylic group.

![Mass spectrum of atomized methyl salicylate](image)

**Figure 14.** Mass spectrum of atomized methyl salicylate (y-axis in arbitrary units).

The AMS spectrum of Malathion is shown in Figure 15. In this case, the higher mass peaks observed are indicative of Malathion. The base peak in the spectrum is $m/z$ 125, a known major fragment from Malathion. Other major ions observed include $m/z$ 55, 63, 79, 93, 99, 143, 158, and 173. Many of these ions are known fragments from Malathion in electron impact mass spectrometry.
Figure 15. AMS mass spectrum of the Malathion.

4.2 MASS DISTRIBUTION OF ATOMIZED METHYL SALICYLATE AND MALATHION

As discussed in Section 2.2, the TOF mode of operation of the AMS gives information on the velocity distribution obtained for aerosol particles as they accelerate from the aerodynamic lens into vacuum, hence, the logging software is capable of deriving the mass as a function of particle size. The time taken between impaction on heater and the detection of resultant ions is small (order of microseconds) compared to the milliseconds taken by particles to travel the length of the TOF region. A measurement of how the reported signal is distributed over particles times of flight can be obtained by summing up the signals in each $m/z$ channel over many chopper cycles. These data are then used to calculate the mass distributions for a particular chemical as a function of
aerodynamic diameter as the time of flight is dependent on the particle’s aerodynamic
diameter. The distributions produced in this mode of operation are normally offset from
the zero line due to the signal produced by background gases. This offset can be
determined by averaging the signal at regions of the distribution where aerosol particles
should not exist. These regions are found at the beginning and end of the distribution and
correspond to particle diameters that are too small or large to be expected.

The $m/z$ channels chosen for the determination of the total organic distribution
must have high signal to noise and must correctly represent the behavior of the total
organic loading (Allan et al., 2004). The $m/z$ channels chosen to study organic chemicals
in TOF mode typically include 41, 43, 44, 45, 55, 57, 69, 71 and 91 based on the fact that
these are prominent organic peaks in ambient mass spectra and are expected to arise from
chemical species such as alkanes, carboxylic acids, alcohols and aromatics (McLafferty
and Turecek, 1993), which have been observed in ambient particles using other methods
(e.g. Saxena and Hildemann, 1996; Fuzzi et al., 2001).

The mass distribution of atomized polydisperse MES particles detected by the
AMS using two fragment ions, $m/z$ 18 and $m/z$ 120 is shown in Figure 16. Mass-to-charge
18 is seen to be the largest intensity peak (ion counts of $10^6$ Hz) and so yields the
smoothest mass distribution. It should be noted that for real samples, $m/z$ 18 would not be
a feasible way of sizing particles because of the presence of actual water in the
atmosphere; $m/z$ 120 would be a better alternative even though it is a less sensitive
fragment ion.
Figure 16. Mass distribution of atomized methyl salicylate particles (y-axis in arbitrary units).

The mass and number distributions (again these should be quantitative) obtained from the atomized Malathion sample using the AMS are displayed in Figure 17. In this mode, the arrival time of ions of individual $m/z$ peaks were monitored and are representative of the particle aerodynamic diameter using a calibration curve. For Malathion, we used $m/z$ 93, 99, 125, and 158 to size particles. The black line (left axis units) shows the mass distribution of the particles with units in bits while the gray histogram (right axis units) shows particle counts detected.
4.3 COMPARISON OF AMS SPECTRA OF METHYL SALICYLATE AND MALATHION WITH NIST DATABASE

The use of a standard quadrupole mass spectrometer with a 70 eV EI ion source is an important property of the AMS design. As this is already a very well established technique in mass spectrometry (McLafferty and Turecek, 1993), it should mean that any mass spectra generated should be similar to the mass spectra held in libraries such as that of the National Institute of Standards and Technology (NIST) (Linstrom and Mallard, 2003). The one technical difference between the AMS and standard gas-phase mass spectrometers is the addition of the heated surface to the ionization region. This may cause differences in the mass spectra produced in two ways.

Firstly, the fact that the molecules being studied spend time in contact with the heated metal surface means they may either undergo changes to their structure in the
process of being vaporized, fragment slightly differently due to the increased amount of
internal energy they possess or cause larger numbers to be released from the first dynode
of the multiplier during detection due to their increased velocity. Secondly, the heater
itself has a bias voltage placed on it so that it does not interfere with the ion optics.
However, this bias voltage will affect the electrical potential of the central ionization
region, reducing the energy of the electrons from the 70 eV that is intended, which in turn
may alter the fragmentation of the molecules. For these reasons, it is necessary to acquire
mass spectra of known chemicals to ensure that they compare well with those in existing
databases and if there are any differences, to characterize these and ensure that they do
not impact on the abilities of the instrument (Allan et al., 2004).

The AMS spectra discussed in 4.1 can be compared with the spectra of the
organic compounds obtained from the NIST mass spectral library. Figure 18 shows the
mass spectrum of MES in red (excluding m/z<20) in comparison to the spectrum of MES
from the NIST (in blue). The back-to-back spectrum shows comparable fragmentation
patterns above ~m/z 50. Below that m/z, the AMS spectrum shows significantly higher
intensity for m/z 44 as well as 29.

Figure 19 shows a comparison of the AMS spectrum of Malathion discussed in
Figure 14 (red) with a spectrum of Malathion from the NIST mass spectral library (blue).
It is clear that the high masses detected (above ~79) are indicative of an EI mass
spectrum of Malathion. A number of the lower masses are probably due to the thermal
decomposition of Malathion particles in the AMS due to the high temperature of the oven
(~ 600°C). The thermal breakdown temperature is reported to be 100°C, above which it
will decompose, significantly increasing the risk of explosion.
Figure 18. Methyl salicylate comparison with NIST methyl salicylate (AMS is in red and NIST is in blue).

The decomposition is due to exothermic and autocatalytic reactions that involve rearrangements and polymerization releasing volatile malodorous and inflammable compounds such as dimethyl sulfide (MSDS Malathion ULV, Crop Data Management Systems, Inc.).

The AMS spectrum of atomized Malathion is reasonably comparable to traditional EI spectra of Malathion from NIST library despite the difference in vaporizer temperature.

Figure 20 shows the AMS mass spectrum of oleic acid (in red) in comparison to the spectrum of oleic acid from the NIST (in blue). The base peak in the spectrum is $m/z$ 41, a known major fragment of oleic acid. Other major ions observed include other typical fragments of long-chain hydrocarbons $m/z$ 29, 55, 60, 69, 73, 83, 97, 111, 129, 152, and 185.
Figure 19. Malathion comparison with NIST Malathion (AMS is in red and NIST is in blue).

Figure 20. Oleic acid comparison with NIST oleic acid (AMS is in red and NIST is in blue).

4.4 ADSORPTION OF ORGANIC MOLECULES ON MINERAL DUST

The spectrum of uncoated zeolite dust particles is displayed in Figure 21. This is presented in a logarithmic form in order to view the difference when organics are coated onto it. Not much particulate mass is detected directly from the zeolite material as expected. However, small signal is detected at m/z 18 and 44 is not surprising due to the
channel dimensions of type A zeolite that allows its usage as an adsorbent for selective removal of certain molecules like H₂O, CO₂, SO₂, and H₂S from mixtures.

Figure 21. Mass spectrum of zeolite dust.

Because the background ion peaks on zeolite dust are low when analyzed by the AMS, the presence of adsorbed organic species on the dust particles is clearly observed. Hence, the presence of adsorbed Malathion on zeolite is observed in the difference between spectra in Figures 21 and 22 and the resulting spectrum is shown in Figure 23 and Figure 24 shows dust coated with oleic acid. As seen on Figure 4.9, m/z 63, 79, 99, 125, 158, 173, 211, and 285 not observed in Figure 21 are typical of NIST database malathion in blue (Fig. 18). It is also observed in Figure 24, the fragment ions of m/z 29, 55, 60, 69, 73, 83, 97, 111, 129, 152, and 185 typical of oleic acid.
Figure 22. Mass spectrum of zeolite dust coated with Malathion.

Figure 23. Difference mass spectrum between Figure 21 and 22.
The mass distribution of zeolite dust coated with methyl salicylate using $m/z$ 18 and 120 is shown in Figure 25. Fragment ion 18 was chosen being the most abundant and 120 because it is the base peak. The distribution shows that the AMS is detecting particles up to ~3 µm in size, although the instrument inlet is very inefficient at that size range (~50% size cut @ 1 µm).

Figure 26 shows the size distribution of zeolite dust coated with Malathion using $m/z$ 18 and 125. And lastly, Figure 27 shows the size distribution of zeolite dust coated with oleic acid using fragment ions 41 and 55; $m/z$ 18 is not used in this case because the signals obtained were low, hence, the base peak 41 and $m/z$ 55 were the most abundant and they were used for this purpose.
Figure 25. Mass distribution of coated MES on zeolite dust using the same two \( m/z \) ratios.

The base peak in the spectrum is \( m/z \) 41, a known major fragment of oleic acid. Other major ions observed include \( m/z \) 43, 54, 62, 79, 93, 99, 127, 143, 158, and 173, many of which are known fragments from oleic acid electron impact mass spectrometry as shown in Figure 19 (blue spectra). The mass distribution is noticed to give some negative values; this could be due to the resolution problems encountered with the AMS during the period of gathering Malathion data.

For the experiments described, using a basis of an inlet flow rate of 1.2 cm\(^3\)sec\(^{-1}\), and equations explained in Section 2.3, the ionization efficiencies obtained for Malathion, methyl salicylate and oleic acid were 5.89\times10^{-5}, 1.15\times10^{-6} and 1.62\times10^{-5} respectively.
Figure 26. Mass distribution of coated Malathion on zeolite dust.

Figure 27. Mass distribution of coated oleic acid on zeolite dust.
The data acquisition software calculates these by plotting fragment ions of choice (in this case, I used the most abundant peak (base peak) as the basis of computation for each; 125\(m/z\) for malathion (65\(m/z\) was plotted for comparison), 120\(m/z\) for methyl salicylate, and 41 (55 was added for comparison) for oleic acid and then sums it up over a range of TOF peaks chosen during data collection (64-125 \(m/z\) for methyl salicylate, 41-55\(m/z\) for oleic acid, and 66-173\(m/z\) for Malathion) and then divides it by the values for the peaks used in order not to account for these twice (Appendix A for details).

The corresponding mass concentrations obtained using the base peak 125, 120, and 41, respectively, was 0.69 \(\mu g\) m\(^{-3}\) for Malathion, 16.29 \(\mu g\) m\(^{-3}\) for oleic acid, and 2.12 \(\mu g\) m\(^{-3}\) for methyl salicylate. Detailed sample calculations for mass concentrations and the limit of detection may be found in the Appendix A and B and the data for each of these species are plotted on Table B-1.
5.1 SUMMARY OF THE OBJECTIVES AND EXPERIMENTS

The focus of this thesis was to obtain a clearer understanding of the fundamental chemistry behind the measurement approach of the Aerosol mass spectrometer, especially as applicable to detecting organic molecules on the surface of particulates, while the particle core are not the primary focus. In addition, to attempt to study low volatile organic type species whose occurrences are transient in the atmosphere.

The AMS provides a combination of quantitative size and chemical analysis of sub-micron aerosol mass loadings with fast time. Other aerosol instrumentation can provide complementary information. For example, differential mobility analyzers count and size ultrafine particles (no chemical analysis), which often have too little mass for effective AMS detection. Laser ionization based time-of-flight particle mass spectrometer systems obtain mass spectra of individual (> 0.2 μm) particles, enabling separation of internal vs. external chemical mixing, but lack quantitative analysis due to non-linearities in the laser-ablation/ionization process.

The Aerodyne AMS is the only currently available instrument capable of providing quantitative size and chemical mass loading information in real-time for non-refractory sub-micron aerosols. The Q-AMS has not been utilized for investigation of pesticides adsorbed on the surface of solid particles previously.

In this study, results have been presented to show that characterization and detection of organic species adsorbed onto inorganic dust particles is possible using Q-AMS. The spectra obtained give mass spectrometric signatures of organic compounds
coated on inorganic particles without detection of particle core; making it possible to identify organic contaminants present in ambient air when adsorbed onto dust particles. Q-AMS can aid in monitoring concentrations of pesticides and similar compounds on dust-type materials with µg m⁻³ concentrations.

One important feature of the AMS is the ability to equate an ion rate detected in the mass spectrometer to a mass concentration for any given chemical species in a sample making use of its ionization efficiency.

Furthermore, we have shown by the experiments described and results obtained therein that the detection and characterization of organic species adsorbed onto inorganic dust particles is possible at µg m⁻³ concentrations using the AMS.

5.2 FUTURE WORK

In the future, more investigations into the coating of pesticides should explore the light scattering module that has recently been developed to be coupled to the AMS (called LS-AMS). This would provide for similar estimations of particle density in real-time, and allow the sizing of refractory particles that would otherwise escape chemical detection (Cross, 2007). The scattered light signals are used to trigger the acquisition of single particle mass spectra, enabling a more efficient operation of the AMS as a single particle detector.

The work presented made use of organic molecules with vapor pressures in the range of 10⁻² to 10⁻⁷. Exploring much lower vapor pressure pesticides like Glyphosphate and other pesticides types like Organochlorines would help provide more data to draw more conclusions of the behavior of these species when coated onto particle supports. Variation of particle core types is another work of interest.
Coating of multiple organic aerosols at the same time on particle support is also a feat to analyze. This has started already in an experiment carried out to coat PSLs and Malathion on zeolite, the spectra obtained is shown in Figure C-1 of Appendix C. It would be very interesting to investigate into the lifetime of vapors as they coat onto dust.
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Liu, B. Y. H., Ziemman, P. J., Kittelson, D. B., and McMurry, P. H.: Generating


Spray Drift Task Force: A summary of aerial application studies, airblast application studies and ground application studies (available from David Johnson at Stewart Agricultural Research Services, Inc., PO Box 509, Macon, MO 63552, USA), 1997.


APPENDICES
Appendix A: Ionization efficiency for methyl salicylate, oleic acid and Malathion

After obtaining sufficient signal from generated aerosols using the AMS, an automated command in the data acquisition software can be used to perform the ionization efficiency (IE) calculations. Typical plots generated using IGOR Pro ionization efficiency panel is given in Figures A-1, A-2, A-3 and A-4; showing ionization efficiency results obtained for methyl salicylate, oleic acid, Malathion and ammonium nitrate respectively.

The linear relationship of the ionization efficiency with the size of the molecule is the basis of the quantification of unknown samples in the AMS. In the equations given in sections 2.3 (as used in Appendix B), an ionization efficiency is required, which is specific to the chemical species being measured. However, it is impractical to experimentally determine specific values of IE for each species and each experiment. Normally, only the value for nitrate $IE_{NO_3}$ is routinely measured (calculated using IGOR; see Figure A-4). The calibrated value of $IE_{NO_3}$ can also be applied to other chemical species, negating the need to perform $IE$ calibrations for multiple chemicals. The assumption is that the ionization cross-section of the parent molecules is proportional to the number of electrons present (Jimenez et al., 2003a) which in turn is a close approximation proportional to the molecular weight, the following generalization is given in Equation 7;

$$\frac{MW_s}{IE_s} = \frac{1}{K_c} \cdot \frac{MW_{NO_3}}{IE_{NO_3}}$$
As described above, ammonium nitrate is used as the primary mass calibration species because the ionization efficiency, density, and shape are well known, and ammonium nitrate does not leave residue to interfere with subsequent measurements. Also, ammonium nitrate vaporizes with close to 100% efficiency and it is well-focused by the aerodynamic lens so that all the particles can be detected.

The ionization efficiency for nitrate ($IE_{NO_3}$) is calculated by determining the number of ions produced per particle of a select size as shown in Equation 12 below (Section 2.4 of the text);

$$IE_{NO_3} = \frac{IPP \times \frac{MW_{NO_3}}{NA}}{6 \times d_m^3 \times \rho \times 1 \times e^{-21 \times \chi_p \times f_{NO_3}} \times f_{NO_3}}$$

where $IPP$ is “Ions produced per particle” determined during the calibration by dividing the sum of all nitrate ions by the total number of detected particles, $d_m$ is the mobility diameter of the DMA size selected particles (350 nm), $\rho$ is the density of the NH$_4$NO$_3$ particles (1.72 g/cm$^3$), and $\chi_p$ is a shape factor (0.8), $f_{NO_3}$ is the fraction of NO$_3$ in NH$_4$NO$_3$ (0.775) and $N_A$ is Avogadro’s number.

As shown in Figure A-1, the dots are ionization efficiency values for particles. The number 4275 is the run number for the experiment for which the values were obtained, numbers 65 and 152 are the $m/z$ used; this can be related to Figures A-2 to A-4 in the same manner. Sample values from these plots from IGOR pro are presented in Tables A-1 to A-3.
Figure A-1. Ionization efficiency for methyl salicylate.

Table A-1 Tabulated Results for Methyl Salicylate Ionization Efficiency

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Run #</th>
<th>m/z used</th>
<th>Ionization Efficiency TOF (m/z)</th>
<th>Ionization efficiency Total</th>
<th>MS Air Beam (Hz)</th>
<th>IE/AB</th>
<th>Peak Range</th>
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</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>4260</td>
<td>30,46</td>
<td>1.84×10⁶</td>
<td>1.84×10⁶</td>
<td>5.792×10⁶</td>
<td>3.18×10⁻¹³</td>
<td>102-122</td>
</tr>
<tr>
<td>Methyl Salicylate</td>
<td>4275</td>
<td>65,152</td>
<td>1.15×10⁶</td>
<td>2.41×10⁴</td>
<td>3.282×10⁶</td>
<td>7.36×10⁻¹¹</td>
<td>64-125</td>
</tr>
</tbody>
</table>
Figure A-2 Ionization efficiency for oleic acid.

Table A-2 Tabulated Results for Oleic Acid Ionization Efficiency

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Run #</th>
<th>m/z used</th>
<th>Ionization Efficiency TOF (m/z)</th>
<th>Ionization efficiency Total</th>
<th>MS Air Beam (Hz)</th>
<th>IE/AB</th>
<th>Peak Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>4317</td>
<td>30,46</td>
<td>5.64×10⁻⁵</td>
<td>6.54×10⁻⁵</td>
<td>7.3×10⁶</td>
<td>8.96×10⁻¹²</td>
<td>46-108</td>
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<tr>
<td>Oleic Acid</td>
<td>4182</td>
<td>41,55</td>
<td>1.62×10⁻⁵</td>
<td>5.44×10⁻⁵</td>
<td>4.98×10⁶</td>
<td>1.09×10⁻¹ⁱ</td>
<td>41-93</td>
</tr>
</tbody>
</table>
Figure A-3 Ionization efficiency for Malathion.

Table A-3 Tabulated Results for Malathion Ionization Efficiency

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Run #</th>
<th>m/z used</th>
<th>Ionization Efficiency TOF (m/z)</th>
<th>Ionization efficiency Total</th>
<th>MS Air Beam (Hz)</th>
<th>IE/AB</th>
<th>Peak Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>4317</td>
<td>30,46</td>
<td>6.54×10⁻⁵</td>
<td>6.54×10⁻⁵</td>
<td>1.05×10⁵</td>
<td>8.96×10⁻¹²</td>
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<tr>
<td>Malathion</td>
<td>4318</td>
<td>125,173</td>
<td>5.89×10⁻⁵</td>
<td>1.73×10⁻⁵</td>
<td>9.37×10⁵</td>
<td>1.847×10⁻¹¹</td>
<td>66-173</td>
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Figure A-4 Ionization efficiency for ammonium nitrate.
Appendix B: Mass concentration calculations and detection limits

As discussed in Section 2.3, a very important feature of the AMS is the ability to equate the detected ion rate in the mass spectrometer to a mass concentration of the chemical species in a sample. Equation 4 was presented by Jimenez et al. (2003) and it is used to convert the ion rate signal, \( I \) in detected ions per second or Hz to an equivalent mass loading or concentration, \( C \) in \( \mu g \ m^{-3} \):

\[
C = \frac{10^{12}}{IE} \frac{1}{Q} \frac{MW}{NA} I
\]

where \( MW \) (g mole\(^{-1}\)) is the relative molecular weight of the parent species, \( I \) (Hz) is the ion rate, \( Q \) (cm\(^3\) s\(^{-1}\)) is the volumetric flow rate into the instrument, \( NA \) is Avogadro’s number \((6.022 \times 10^{23} \) mole\(^{-1}\)) and \( IE \) is the ionization efficiency, a dimensionless quantity equaling the ratio of ions detected by the multiplier to the number of available desorbed molecules of the parent chemical species in the detection region. Note that the \( IE \) depends on the probability of producing a positively charged ion from a vapor molecule, the transmission efficiency of the ions passing through the quadrupole and the detection efficiency of the electron multiplier. The factor of \( 10^{12} \) is included to make the conversion from g cm\(^{-3}\) to \( \mu g \ m^{-3} \).

All results were obtained using the data of the base peak; \( m/z \) 120 for Methyl Salicylate, \( m/z \) 125 for Malathion and \( m/z \) 41 for oleic acid for calculations. The ion rate, background signals and the AMS inlet flow rates are read off from IGOR program upon loading of experimental runs. Ionization efficiency is read off from the graphs provided in Appendix A-1 to A-4.
Table B-1. Tabulated Results for Mass Concentration and Detection Limits

<table>
<thead>
<tr>
<th></th>
<th>Molecular Weight, MW (g mol⁻¹)</th>
<th>IE x10⁻⁶</th>
<th>Flow Rate, Q (cm⁻³ sec⁻¹)</th>
<th>Ion Rate, I (Hz) x10⁴</th>
<th>Background (Hz)</th>
<th>Mass Concentration (µg m⁻³)</th>
<th>Detection Limit, DL (µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Salicylate</td>
<td>152.15</td>
<td>1.15</td>
<td>1.25</td>
<td>1.207</td>
<td>463.31</td>
<td>2.12</td>
<td>0.011</td>
</tr>
<tr>
<td>Malathion</td>
<td>330.36</td>
<td>58.9</td>
<td>1.23</td>
<td>19.9</td>
<td>15700</td>
<td>1.51</td>
<td>0.017</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>282.47</td>
<td>16.2</td>
<td>1.051</td>
<td>59.3</td>
<td>7100</td>
<td>16.29</td>
<td>0.007</td>
</tr>
</tbody>
</table>
Sample Calculations for Methyl Salicylate

Mass Concentration: Using the following parameters (as shown on Table A-4);

Molecular weight, \( MW = 152.15 \text{ g mole}^{-1} \)

Ion Rate, \( I = 1.207 \times 10^4 \text{ Hz} \)

Ionization efficiency, \( I.E = 1.15 \times 10^{-6} \)

Flow rate, \( Q = 1.25 \text{ cm}^3 \text{s}^{-1} \)

Avogadro’s number, \( N_A = 6.02 \times 10^{23} \text{ mole}^{-1} \)

Mass Concentration, \( C = \frac{10^{12} 1 MW}{IE Q N_A I} \)

\[
C = \frac{(152.15 \text{ g mole}^{-1}) \times (1.207 \times 10^4 \text{ s}^{-1})}{1.15 \times 10^{-6} \times (1.25 \text{ cm}^3 \text{s}^{-1}) \times (6.02 \times 10^{23} \text{ mole}^{-1})} \times \frac{(100 \text{ cm})^3}{(1 \text{ m})^3} \times \frac{(1 \mu g)}{(10^{-6} \text{ g})} \\
= 2.12 \mu g \text{ m}^{-3}
\]

Detection limit:

Because a finite number of randomly generated ions are being detected, there will be an intrinsic variability in the average number detected. As the number of available molecules is high but the probability of successfully ionizing and detecting a specific molecule is low, it can be assumed that the probable distribution of numbers detected for a given population can be modeled as a Poisson distribution; the probability of producing and detecting multiple ions from a single molecule is considered lower still.

Assuming a Poisson distribution,

\[
P(k, a) = \frac{e^{-a} a^k}{k!}
\]
(Harris et al, 1974), for which the mean and variance are both equal to the ‘a’ parameter; the variance of the blank can be approximated by the average ion rate of the background signal at the mass that is being used for the calculations. The standard deviation of the blank is thus $s_{\text{blank}} \approx \sqrt{a}$, the limit of detection is the concentration that produces a signal that is 3 times the standard deviation of the blank, $3s_{\text{blank}}$.

The values for signal and background from in Table A-4 for methyl salicylate are: ion rate signal, $I = 1.207 \times 10^4$ Hz, and background signal, $a$ (Hz) = 463.31. The mass concentration was $C = 2.12$ µg m$^{-3}$ for these data. The standard deviation of the “blank” is

$$s_{\text{blank}} \approx \sqrt{463.31} = 21.52$$

The concentration detection limit for $3s_{\text{blank}}$ is thus

$$DL = \left( \frac{C}{I} \right) \times 3s_{\text{blank}} = \frac{2.12 \mu g \ m^{-3} \times 3 \times 21.52 \text{s}^{-1}}{1.207 \times 10^4 \text{s}^{-1}} = 0.011 \mu g \ m^{-3}$$
Appendix C: Mass distribution for polystyrene latex and Malathion

Figure C-1 shows the mass distribution of the growth of organic aerosols as PSLs is been coated with Malathion. Polystyrene latex (PSL) spheres are particles of known size mostly used for particle size calibrations as primary size standards were used for this experiment. PSLs can be purchased with specific and traceable diameters, are spherical and have a density close to unity (1.05 g cm\(^{-3}\)), making calculations much easier and much less prone to uncertainties. As the PSL is less volatile than other chemicals normally vaporized by the instrument, the oven temperature must be increased to at least 800 °C to ensure rapid vaporization and adequate particle sizing.

PSL size 350nm was used; \( m/z \) 104 (styrene parent ion) in red, is seen to grow up to over 1000nm (1µm) as the base peak of Malathion is been coated onto it.