**Usage of Aerosol Mass Spectrometry for the Measurement of
the Physical and Chemical Properties of the Atmospheric
Nanoparticles**

A Dissertation

Presented to

The Academic Faculty

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

In the Department of Chemical Engineering

By

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March, 2010

Acknowledgements

First of all I would like to thank my advisor, Spyros N. Pandis, for giving me the opportunity to work with him. He gave me an excellent guidance and the chance to visit Carnegie Mellon University and collaborate with distinguished scientists. I would also like to thank all the members of the general Pandis group with whom I enjoyed working with, and especially Mihalis Pikridas, Magda Psychoudaki, Dr. Christos Fountoukis, Gabriella Engelhart, Byong-Hyoek Lee, Lea Hildebrandt and Dr. Ravi Pathak. Also I would like to thank Dr. Nikos Mihalopoulos and his group and especially Dr. Katerina Bougiatioti and Dr. George Kouvarakis for their hospitality and help during the FAME campaigns. Finally, I would like to thank my parents Gavriil and Lambrini, my brothers Dimitris and Petros and also Dimitris who always supported me.

Abstract

The overall objective of this dissertation is to improve our understanding of the organic and inorganic atmospheric particles combining laboratory and field studies and state-of-the-art instrumentation. The recent development of on-line aerosol mass spectrometry and other continuous techniques allows for the first time detailed high time resolution investigations of atmospheric particulate matter and its chemical and physical properties (e.g. volatility, density etc).

Organic aerosol (OA) consists of compounds with a wide range of volatilities and its ambient concentration is sensitive to this volatility distribution. Recent field studies have shown that the typical mass spectrum of ambient oxygenated organic aerosol (OOA) as measured by the Aerodyne Aerosol Mass Spectrometer (AMS) is quite different from the secondary organic aerosol (SOA) mass spectra reported in smog chamber experiments. Part of this discrepancy is due to the dependence of SOA composition on the organic aerosol concentration. High precursor concentrations lead to higher concentrations of the more volatile species in the produced SOA while at lower concentrations the less volatile compounds dominate the SOA composition. α -pinene, β -pinene, d-limonene and β -caryophyllene ozonolysis experiments were performed at moderate concentration levels. Using a thermodenuder the more volatile SOA species were removed achieving even lower SOA concentration. The less volatile fraction was then chemically characterized by an AMS. The signal fraction of m/z 44, and thus the concentration of CO_2^+ , is significantly higher for the less volatile SOA. High NO_x conditions result in less oxidized SOA than low NO_x conditions, while increasing relative humidity levels results in more oxidized products for limonene but has little effect on α - and β -pinene SOA. Combining a smog chamber with a thermodenuder model employing the volatility basis-set framework the AMS SOA mass spectrum for each

experiment and for each precursor is deconvoluted into low, medium and high volatility component mass spectra. The spectrum of the surrogate component with the lower volatility is quite similar to that of ambient OOA.

The density of organic aerosol is another poorly-characterized property and there is still no general method for its estimation in aerosol systems with size-dependent composition where the organic-inorganic fraction changes fast. An algorithm for the calculation of organic aerosol density in mixed organic-inorganic particles combining measurements by the AMS and the Scanning Mobility Particle Sizer (SMPS) was developed. The approach is applicable to particles with size-dependent composition. The estimated density of secondary organic aerosol (SOA) formed by α -pinene, β -pinene and d-limonene ozonolysis was in the range of 1.4-1.65 g cm⁻³. However, in two cases the SOA had much lower density (0.9-1.0 g cm⁻³) indicating that there may be changes in particle morphology depending on the conditions of SOA formation. The high estimated density for these systems suggests that SOA particles may be solid or waxy. Based on our results, SOA yields in smog chamber experiments may be a lot higher (up to 50%) than the currently assumed values. Most of the literature results have been calculated by measuring the SOA number distribution with an SMPS and then multiplying the volume concentration with a density equal to 1 or 1.2 g cm⁻³. This method is also applicable to the primary organics and to ambient particles assuming that these particles are close to spherical and can also provide the collection efficiency (CE) of the AMS. For example this approach was used for field data during the Finokalia Aerosol Measurement Experiments (FAMEs).

Real-time measurements of non-refractory submicron aerosols (NR-PM₁) were conducted during the FAME-08 (early summer 2008) and FAME-09 (winter 2009) field studies. Both campaigns were part of the intensive EUCAARI Pan-European campaigns.

The Finokalia site, located at a remote coastal place on Crete (Greece), is isolated and away from anthropogenic sources of pollution and this allows the study of aged organic aerosol coming from different directions. In order to measure the size-resolved chemical composition of the NR-PM₁ particles an AMS was used. During FAME-08 ammonium sulfate and ammonium bisulfate were the largest components of the NR-PM₁, followed by organics and water. There was practically zero nitrate. The organic aerosol was mainly regional, since the total organic aerosol mass changed little with source region. During FAME-09 organics, ammonium sulfate and ammonium bisulfate had almost equal fractions with the organics, but the nitrate was very low. The aerosol concentrations were almost a factor of 3 lower in FAME-09 than in FAME-08 but more variable. A thermodenuder coupled with the Q-AMS and an SMPS were operated as well. We used the algorithm that combines AMS and SMPS measurements to estimate the AMS CE and organic particle density both for ambient and thermodenuder samples. Using these values the concentrations measured by the AMS for the ambient particles were in a good agreement with the other independent concentration measurements (filters, steam sampler).

The Finokalia Station is ideal for studying organic aerosol of different photochemical age. The site is isolated, away from human activities and the wind may come from various directions: Europe, Balkans, Africa and sea. Further, the oxidation levels can vary, being stronger in the summer and weaker during winter. This allows the investigation of particles originating from the same sources but transferred under different metrological and photochemical conditions. The AMS-SMPS thermodenuder system was employed as well, for organic aerosol volatility measurements. For the volatility corrections we used the organic density and the CE of the AMS both of ambient and thermodenuded aerosol as calculated by the algorithm that combines AMS

and SMPS data. The organic aerosol sampled during FAME-08 is quite uniform and highly oxidized more than one order of magnitude less volatile than laboratory-generated α -pinene SOA.

The final goal of this research is to expand methods for measurement of the semi-volatile inorganic species of atmospheric aerosol and the gases that are in equilibrium with them. Modifying the steam jet aerosol collector (SJAC) technique both particulate phase (e.g. sulfate, nitrate, chloride, ammonium) and gas phase (e.g. ammonia, nitric acid, nitrous acid) can be measured. For this approach a denuded (from the gas species) and an undenuded line are used. From their difference the gas phase contribution can be estimated. Evaluating this system in an agricultural environment the concentrations of NH_3 , HONO , and HCl were measured. The HNO_3 concentration was close to the detection limit (0.5 ppb) of our system.

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Chapter 1

Introduction

1.1 Atmospheric Aerosols

Aerosols are particles suspended in the atmosphere with diameters between 1 nm and approximately 50 μm . Usually their volume or mass distribution is described by 2 modes (Figure 1.1): the accumulation mode (from ~ 0.1 to ~ 2 μm) and the coarse (from ~ 2 to ~ 50 μm) mode. The accumulation mode consists of combusting particles, secondary organic particles, nitrates and sulfates. The coarse mode usually is characterized by particles produced by mechanical processes (dust, salts, pollen etc). Atmospheric particles may contain non-volatile and semi-volatile compounds and mainly consist of sulfates, nitrates, ammonium, dust, water, metals and organic matter. A typical mass distribution and chemical composition is shown in Figure 1.2. The chemical composition depends on the area e.g. urban, rural or remote. Depending on the relative humidity (RH) aerosols can either be in a solid, liquid or mixed phase. Atmospheric particles are also known as particulate matter (PM).

Figure 1.1: Typical volume distributions of atmospheric particles with the different modes.

Figure 1.2: Typical mass distribution and chemical composition of atmospheric particles (Los Angeles, 1987). The accumulation mode mainly consists of sulfate, nitrate, ammonium and organics and the coarse mode is characterized by sodium, chloride, nitrate and some sulfate.

Aerosols, also referred as particulate matter (PM), are classified as primary and secondary. Primary PM is emitted directly in the particulate phase (solid or liquid) from transportation, industry, power generation, wood burning and natural sources such as dust and sea salt. Secondary PM is reaction products of gases mainly SO_2 , NO_x , NH_3 , and volatile organic compounds (VOCs).

1.2 Atmospheric Particles and their Role

Atmospheric particles can have a significant impact on physical and chemical processes in the atmosphere even at low concentrations. First, they can have major adverse effects on human health. Dockery et al. (1993) showed that high concentrations of ambient particles with a diameter smaller than $2.5\text{ }\mu\text{m}$ ($\text{PM}_{2.5}$) can cause even death to susceptible populations. Several studies correlated the PM concentrations to decreased lung functions (Gauderman et al., 2000), incidents of bronchitis (Dockery et al., 1996) and overall hospital admissions for respiratory ailments (Pope, 1991). A second effect is the aerosols' impact on earth's radiation balance and climate. Ambient particles can absorb light (e.g. particles composed of elemental carbon, EC) and have a warming effect on climate. On the other hand, particles scatter light and have a cooling effect on the climate. However, atmospheric aerosols may contain various components, so they are chemically complex and often have both absorptive and scattering properties. The net effect is a cooling one (Seinfeld and Pandis, 2006).

The ambient particles do not affect the radiation balance and climate only directly, but also indirectly. They function as nuclei upon which cloud droplets can form. The number and the size of the cloud droplets for a given supersaturated environment is determined by the size distribution and chemical composition of the aerosol (Lohmann et al., 1999). Thus both albedo, which is the fraction of incident solar radiation that is reflected back into the space, and cloud lifetime is affected by particulate pollution levels (Haywood and Boucher, 2000).

One more phenomenon caused by atmospheric particles is the reduction of the visibility. Particles reduce visibility and contribute to the “haze” associated with the urban pollution.

Because of all the above reasons the study of the atmospheric particles is important for both air quality and climate change. Despite the recent progress there are still major gaps concerning the chemical and physical properties of the atmospheric aerosols. More investigations with new instrumentation and methods will help us to understand their properties, sources, atmospheric processes and their overall role better and to eliminate their negative effects.

1.3 Secondary Organic Aerosol (SOA) and its Properties

SOA may be produced by either anthropogenic or biogenic precursors. Emissions of biogenic volatile organic compounds (VOCs) exceed anthropogenic on both continental and global scales (Rasmussen, 1972; Zimmerman et al., 1978; Guenther et al., 1995). Monoterpenes represent about 10% to 50% of the biogenic non-methane hydrocarbon emissions (Lamb et al., 1987; Müller, 1992; Guenther et al., 1995). These compounds are highly reactive and can be oxidized by ozone, NO₃ and OH radicals (Atkinson, 1997; Jang and Kamens, 1999; Yu et al., 1998; Glasius et al., 1997, 1999a, b, 2000; Koch et al., 2000; Jaoui and Kamens, 2001; Kamens and Jaoui, 2001). Monoterpenes may contribute as much as 50% to the total organic aerosol (Andersson-Sköld and Simpson, 2001). In the US roughly half of the monoterpene emission is α -pinene, β -pinene and d-limonene (Lamb et al., 1993). Thus their study of their chemical and physical properties is very important.

The density of inorganic atmospheric particles is known. For example particles of ammonium nitrate have a density of 1.70 g cm^{-3} , while those of ammonium sulfate 1.77 g cm^{-3} . However, the aerosol organic matter consists of thousands of compounds (alkanes, alkenes, aldehydes, organic acids, ketones, aromatics etc) and only 10-20% can be translated. Thus the estimation of the organic particles' density is difficult. For its calculation an indirect way is usually used: comparing instrumentation that measures the volume and instrumentation that computes the mass of the atmospheric particles.

One significant part of the atmospheric aerosol is semi-volatile compounds. The semi-volatile compounds are compounds that are transferred continuously between gas and particle phase. The most important inorganic semivolatile compounds are ammonium nitrate and ammonium chloride (Seinfeld and Pandis, 2006). But for the thousands organic components our knowledge is limited. Knowing the partitioning between gas and particle phase the SOA production rate is required for the calculation of their formation rate (Kanakidou et al., 2005). Additionally, estimating the volatility of the atmospheric particles one can get indirect information about their chemical composition.

For many years now the standard chemical analysis of the atmospheric aerosols is conducted with their collection on filter and analysis in the laboratory. But their chemical complexity and unstable nature has motivated research into new real time techniques, avoiding the collection, transportation and storage of samples. In real time measurements one can get more a lot more information than samples collected over hours or days. In addition to the chemical composition, other important parameters include the physical properties of the aerosols such as the number, the volume and the mass distribution, and thus the number, the volume and the mass concentration.

The recent development of the Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000; Jimenez et al., 2003; Allan et al., 2003; Alfarra et al., 2004; Canagaratna et al., 2006) opened new avenues for atmospheric chemistry research. This thesis is based mainly on the AMS. The AMS measures in real time the chemical composition (sulfate, nitrate, ammonium, chloride, water and organics) of the particles, the mass of each species and the mass distributions of the species as a function of the vacuum aerodynamic diameter. This instrument has been used in many field measurements (Edinburgh and Manchester 2000-2001, Pittsburgh 2002, Mexico City 2003, Finokalia 2008 and 2009, Paris 2009) but also in laboratory experiments (Morris et al., 2002; Jimenez et al., 2003; Bahreini et al., 2005). Additionally, measurements were conducted in mobile labs e.g. in Mexico City (Kolb et al., 2004) and in the upper atmosphere of Eastern Asia and Germany (Bahreini et al., 2003; Schneider et al., 2006).

1.4 The Aerosol Mass Spectrometer (AMS)

The AMS (Jayne et al., 2000; Jimenez et al., 2003; Allan et al., 2003; Alfarra et al., 2004; Canagaratna et al., 2006) provides in real time the chemical composition and the mass concentration of the atmospheric aerosols (Figure 1.3). The aerosols enter the instrument through a sampling inlet that restricts the flow with a 100 μm critical orifice and then they pass through the aerodynamic lens which focuses the aerosols into a tight beam. The transmission efficiency is 100% for particles approximately 60-600 nm, but for the range between 20-60 nm and 600-200 nm the transmission is partial. After passing through the lens the aerosols enter the particle sizing chamber and meet a chopper which has a slit and rotates with a frequency of 80-100 Hz. Finally the particles enter the

detection chamber. During this travel, 6 vacuum pumps create very low pressure conditions.

Figure 1.3: Schematic of the Aerodyne AMS.

The AMS can operate in 3 modes. The first mode is the Time-of-Flight Mode (ToF Mode). In this mode the AMS measures the mass distribution as a function of the vacuum aerodynamic diameter (Figure 1.4b). During this operation mode the chopper is in the beam chopped position and the particle beam is blocked most of the time allowing only a small fraction of the particles to pass through and reach the detection chamber (Figure 1.4a). As the particles travel on a straight path through the sizing chamber, they spread out according to their size as a result of the supersonic expansion through the final aperture of the lens, with the smaller particles traveling faster than the larger particles. When the particles reach the detection chamber, the time to travel across the sizing chamber is determined, and from this the particle velocity and aerodynamic diameter are calculated.

Figure 1.4: AMS ToF Mode, where (a) the chopper allows the transmission only of a small part of the aerosol providing (b) the mass distribution of the aerosol.

The second mode is the Mass Spectrum Mode (MS Mode). This mode provides the mass concentration and the mass spectra (Figure 1.5b) and thus the chemical composition of the aerosol. In this case the chopper is in the beam open position (Figure 1.5a), so all of the particles reach the detection chamber. In the detection chamber the particles hit on a heated surface (vaporizer), which is at high temperature (600°). The volatile and semi-volatile portions of the aerosols are vaporized. Next, they are immediately ionized by electron impaction in a custom-built closed source electron impact ionizer/heater assembly (Figure 1.6). A standard quadrupole mass spectrometer detects the positive ion fragments generated by the electron impact ionization. Quick bursts of ions (tens of microseconds in length compared to the 3-4 milliseconds needed to traverse the particle sizing chamber) classify single particle events of sufficient size.

Figure 1.5: MS Mode, where (a) the chopper allows the 100% the transmission of the particles providing (b) the mass spectra.

Figure 1.6: Vaporization of the particles and electron impact ionization.

The third mode is the alternation between the 2 modes described above every 15 seconds and is called Alternating Mode. With this combination the AMS measures simultaneously the chemical composition, the mass distribution for each species (sulfate, nitrate, ammonium, chloride, water and organics) and the mass for each species (Figure 1.7). The time resolution is usually 3 or 5 min.

Figure 1.7: (a) Mass distribution as a function of the vacuum aerodynamic diameter for each species and (b) chemical composition of aerosols.

The AMS does not measure the entire aerosol that enters the instrument, due to the bounces of the less or non volatile particles on the vaporizer (ion collection efficiency ICE) and the partial transmission of the aerosol through the lens (particle collection efficiency, PCE). The ICE depends on the species and the proportion of the compounds in the particle but also on the phase of the particle (solid/liquid). The PCE is a function of the size and the shape of the particles. The ICE and the PCE are related with collection efficiency, CE:

$$CE = ICE \cdot PCE \quad [1]$$

The ion collection efficiency (ICE) can be viewed as a measure of the number of ions that actually reach the AMS detector out of the total number of ions that can be produced of the particles in the instrument. The ICE depends on the ability of the particle to bounce in the AMS vaporizer. In the lab, oleic acid has an ICE of 1 (Allan et al., 2004) while citric acid has an ICE of 0.2 for dry particles and around 0.4 for aqueous (Mathew et al., 2004). The ICE of ammonium sulfate particles varies as a function of relative humidity (0.2 when dry and 1 when aqueous) but ammonium nitrate particles have ICE around 1 both at high and low RH (Mathew et al., 2004). For ambient organics particles internally

mixed with sulfate in the accumulation mode ICE appears to be close to 0.5 (Zhang et al., 2005). Despite these efforts there are still significant uncertainties about the ICE of ambient and laboratory aerosol particles.

Another important parameter is the relative ionization efficiency (RIE) which is the ratio of the electron impact ionization efficiency of a given species to the measured ionization efficiency of nitrate on a per unit mass basis. RIE values of each species are determined using the approach of Jimenez et al. (2003) and Alfarra et al. (2004). For organics the RIE value is 1.4, for sulfate 1.2, and for nitrate 1.1 ($RIE_{\text{nitrate}} = \text{true IE of nitrate} / IE_{\text{nitrate}}$), where the true IE of nitrate is calculated from all fragments produced by nitrate and the IE_{nitrate} is estimated only from the ion fragments 30 (NO^+) and 46 (NO_2^+). For ammonium the RIE is estimated by ionization efficiency calibrations because at the relevant m/z ratios (15 for NH^+ , 16 for NH_2^+ and 17 for NH_3^+) there are significant interferences from CH_3^+ (m/z 15), O^+ (m/z 16) and OH^+ (m/z 17) (Canagaratna et al., 2006). The determination of the mass concentration of each species has been described in detail by Jimenez et al. (2003) and Canagaratna et al. (2006).

The critical equation that AMS software uses to convert the signal to mass is:

$$C_i = \frac{\sum_{\text{all } s} I_{i,s}}{Q N_{\text{AV}}} \frac{MW_{\text{nitrate}}}{IE_{\text{nitrate}}} \frac{1}{RIE_i} \frac{1}{CE_i} 10^{12} (\text{cm}^3 \text{m}^{-3}) (\mu\text{g g}^{-1}) \quad [2]$$

where C_i is the concentration of the compound i [$\mu\text{g m}^{-3}$], $\sum I_{i,s}$ is the total intensity of species I that produces additional ions at s m/z [Hz], Q is the flow rate of the particles at the inlet [$\text{cm}^3 \text{s}^{-1}$], N_{AV} is the Avogadro number (6.02×10^{23} molecules/mol), MW_{nitrate} is the molecular weight of the nitrate (62g mol^{-1}), IE_{nitrate} is the ionization efficiency of the

nitrate [ions molecule⁻¹], RIE_i is the relative (to the nitrate) ionization efficiency of i (dimensionless) and CE_i is the collection efficiency of i (dimensionless).

1.5 Objectives and Scope of this Thesis

The objective of this thesis is to improve our understanding of the physical and chemical properties of atmospheric organic aerosols both in the laboratory and in the actual atmosphere.

In Chapter 2 a new method was introduced in order to deconvolute the mass spectra of biogenic secondary organic aerosol (SOA) according to their volatility. SOA consists of compounds with a wide range of volatilities. Using a thermodenuder the more volatile SOA species evaporate and the remaining less volatile fraction is chemically characterized by an AMS. Combining a smog chamber with a thermodenuder model employing the volatility basis-set framework the AMS, SOA mass spectrum for each experiment and for each precursor is deconvoluted into low, medium and high volatility component mass spectra.

The density of the organic particles has been estimated by several methods. However, there is still no general method for the calculation of the density of organic particulate matter in rapidly varying organic-inorganic aerosol systems with size-dependent composition. In Chapter 3 an algorithm, which takes into account changes in particle composition with size and calculates the density of the organic particles was developed. This algorithm combines mass and volume distributions from an AMS and an SMPS correspondently and can also estimate the collection efficiency of the AMS.

In Chapter 4 the above algorithm was applied to ambient data, obtained from two field campaigns in Crete, FAME-08 and FAME-09. For these field measurements the collection efficiency and the density of organic aerosol for both ambient and the thermodenuded samples are estimated. These values were used to correct the ambient AMS measurements and to evaluate the results against the measurements by traditional techniques.

The information collected was used to gain valuable insights about the volatility of ambient particles in Chapter 5.

Except for the organic material in the atmosphere, inorganic aerosol can also play an important role in the atmospheric chemistry. Several methods have been developed for the online measurements of the inorganic species (e.g. Khlystov et al., 1995; Weber et al., 2001). In Chapter 6 we introduce a new method for semi-continuous measurements of inorganic particles and inorganic gases. The method of Khlystov et al. (1995) was extended using a steam sampler and ionic chromatography for measurements of particulate phase (e.g. sulphate, nitrate, chloride, ammonium etc) and gas phase (e.g. NH_4 , HNO_3 , HNO_2).

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Chapter 2

Mass Spectra Deconvolution of Low, Medium and High Volatility Biogenic Secondary Organic Aerosol

This work has been published as:

Kostenidou, E., Lee, B. H., Engelhart, G. J., Pierce, J. R., and Pandis, S. N. (2009). Mass Spectra Deconvolution of Low, Medium and High Volatility Biogenic Secondary Organic Aerosol, *Environmental Science and Technology*, 41, 4884-4889.

2.1 Introduction

Secondary organic aerosol (SOA) is formed by condensation of low-volatility products of the oxidation of volatile organic compounds (VOCs) on pre-existing particles and is an important contributor to ambient particulate matter in urban, rural and remote areas (Chow et al., 1994; Turpin et al., 1995). Monoterpene SOA can contribute as much as half of the total organic aerosol (Andersson-Sköld and Simpson, 2001) with SOA from α -pinene, β -pinene and limonene often dominating the system as they account for 30-70% of the overall terpene emissions (Guenther et al., 1995; Griffin et al., 1999; Geron et al., 2000; Owen et al., 2001; Seinfeld and Pankow, 2003; Kanakidou et al., 2005).

SOA formation has been studied in environmental chambers for more than 30 years (Grosjean et al., 1989; Stern et al., 1989; Odum et al., 1997; Kamens et al., 1999) focusing mainly on the produced aerosol concentration and yield. In the beginning only organic volume or mass concentration was measured with later studies focusing more on the speciation of the products (Palen et al., 1992; Jang et al., 1999; Sax et al., 2005), but a complete picture of the SOA was missing. High concentrations of precursors have been often used in smog chamber experiments so that the organic aerosol concentration and composition can be monitored with the existing instrumentation, samples can be obtained for chemical analysis, contamination effects can be minimized, reactions can be accelerated so that the experiment can take place in a reasonable timescale, etc.

The recent development of the Aerodyne AMS (Jayne et al., 2000; Jimenez et al., 2003) provides real-time size and composition analysis of aerosol particles and has allowed the characterization of the mass spectra of all the SOA produced in smog chamber experiments (Bahreini et al., 2005; Alfarra et al., 2006). Zhang et al. (2006)

introduced a new technique to deconvolve AMS mass spectra in two components: hydrocarbon-like and oxygenated organic aerosol (HOA and OOA). This approach indicated that the AMS mass spectrum of OOA is similar to that of aged organic aerosol in rural areas, but rather different than that of smog chamber SOA. The OOA mass spectrum is dominated by CO_2^+ (m/z 44), but laboratory SOA mass spectra from α -pinene, β -pinene, limonene and β -caryophyllene have a greater signal at m/z 43 than at m/z 44. This discrepancy potentially puts into question the relevance of the smog chamber experiments for the study of atmospheric SOA and indicates gaps in our understanding of the system.

Organic aerosol consists of species with a wide range of volatilities with the less volatile dominating at low concentrations and the more volatile at high (Donahue et al., 2006; Stanier et al., 2006). The wide range of volatilities reflects the wide range of products that are formed during the oxidation of these rather large organic molecules. The volatility distribution of the resulting SOA is affected by the temperature, the precursor, oxidant, and NO_x levels, and is determined by the oxidation pathways for each precursor. The species of different volatility can be partially separated using a thermodenuder operating at the appropriate temperature (An et al., 2007). In a recent study Lee et al. (2010) investigated the volatility of α -pinene, β -pinene and limonene SOA using a thermodenuder and a Scanning Mobility Particle Sizer (SMPS). They showed that limonene SOA was less volatile, the relative humidity (RH) had a small effect on the SOA volatility, and that the high NO_x conditions produced more volatile α -pinene and β -pinene SOA. The results of their study will be combined here with AMS measurements to investigate the changes in composition of the SOA as its more volatile components are

removed by the thermodenuder. In this work we use medium precursor concentrations in order to produce SOA of both high and low volatility. Using the volatility basis-set (Donahue et al., 2006) we then analyze and compare the AMS mass spectra as a function of the volatility of the products.

2.2 Experimental Approach

SOA was produced by ozonolysis of α -pinene, β -pinene, limonene and β -caryophyllene in the Carnegie Mellon University smog chamber. The experiments were conducted at low (<10%) and intermediate (~50%) RH and at low (<2 ppb) and high (150-200 ppb) NO_x conditions (Table 2.1). 2-butanol in excess (0.5 mL) was used as a radical scavenger. The SOA components were then passed alternatively through the thermodenuder or a bypass line. The sample line was then split and the components were characterized by a quadrupole AMS (Aerodyne) and a SMPS (TSI model 3936). More details about the experimental set up are given by Lee et al. (2010).

Smog Chamber: Experiments were performed in a 10 m³ Teflon reactor (Welch Fluorocarbons). The reactor was first filled with clean air, containing less than 1 cm⁻³ particles and 2-butanol (Sigma Aldrich, purity 99.5%) as OH-scavenger. Then the SOA precursor, α -pinene, β -pinene, d-limonene or β -caryophyllene (Sigma Aldrich, purity 99.9 %) was injected. The hydrocarbon reacted with ozone produced by an ozone generator (Azco HTU500ACPS) and was measured by a continuous ozone analyzer (Dasibi 1008-PC). The temperature in the smog chamber was kept constant at $24 \pm 1^\circ\text{C}$.

Thermodenuder: The thermodenuder of An et al. (2007) was used to separate the aerosol based on its volatility. The temperatures in the thermodenuder were in the range of 25-100°C with a centerline residence time of 16 seconds.

SMPS: The SMPS system (TSI model 3936) operated at a sheath flow rate of 5 L min⁻¹ and at a sample flow rate of 1 L min⁻¹. Assuming spherical particles this instrument provided the volume fraction remaining (VFR) which is the ratio of the aerosol volume in the thermodenuder to the aerosol volume in the smog chamber.

AMS: An Aerodyne AMS (Jayne et al., 2000; Jimenez et al., 2003; Allan et al., 2003; Canagaratna et al., 2006) was used to characterize the chemical composition of SOA during the experiments both directly from the smog chamber and after passing through the thermodenuder.

Table 2.1: Experimental conditions for SOA experiments.

Exp.	Precursor	[Precursor] (ppb)	(O ₃) (ppb)	(NO _x) (ppb)	RH (%)	Maximum Aerosol Conc. ^a (μg m ⁻³)
1	α-pinene	100	1270	<2	<10	111
2	α-pinene	100	1176	<2	<10	136
3	α-pinene	100	1040	<2	53	161
4	α-pinene	100	720	195	<10	68
5	limonene	100	1200	<2	<10	377
6	limonene	100	1050	<2	<10	419
7	limonene	100	1120	<2	52	405
8	limonene	100	890	160	<10	384
9	limonene	100	650	210	<10	272
10	β-caryophyllene	45	1400	<2	<10	126
11	β-caryophyllene	45	660	150	<10	245
12	β-pinene	100	1020	<2	<10	74
13	β-pinene	100	1090	<2	46	69
14	β-pinene	100	700	200	<10	179

^a Aerosol mass concentration from SMPS data assuming a density of 1.5 g cm⁻³.

2.3 Data Analysis

Our analysis requires the composition of the SOA (mass fractions of high, medium and low volatility components) exiting the thermodenuder at different temperatures. To calculate this composition two different models are used. First, using the volatility basis-set approach (Donahue et al., 2006) we estimate the composition of the aerosol exiting the smog chamber and entering the thermodenuder. Then, we simulate the evaporation of the organic aerosol in the thermodenuder with the model of Lee et al. (2010) and estimate the aerosol composition remaining after the thermodenuder as a function of its volatility. Finally the AMS mass spectrum is deconvoluted into three mass spectra according to volatility. These modeling tools are described below.

2.3.1 Smog Chamber Model

This model simulates the SOA production during the smog chamber experiments. As inputs it uses the mass yields for each surrogate SOA component. These mass yields have been calculated in previous studies by fitting smog chamber experiments using the 4-component basis-set (Pathak et al., 2007; Zhang et al., 2006). The other inputs in this model are the smog chamber temperature and the reacted precursor concentration. The model solves a system of equations describing the equilibrium partitioning (Seinfeld and Pandis, 2006) of the 4-surrogate species of the volatility basis-set (VBS). The output of this model is the concentrations of the VBS surrogate species with effective saturation vapor concentrations 1, 10, 100 and 1000 $\mu\text{g m}^{-3}$ in the gas and particle phases entering the thermodenuder. The effective saturation concentration C^* in the volatility basis set is defined as the effective saturation concentration of this surrogate compound at 298 K

(Donahue et al., 2006). In some sense the C^* at 298 K is the “name” of this surrogate species and does not change if the temperature changes. However, the actual effective saturation concentration of the surrogate species does change with temperature according to the Clausius-Clapeyron equation. In this paper, we will always refer to the surrogate species in a volatility bin by using its C^* at 298 K.

2.3.2 Thermodenuder Model

This model describes the evaporation of the SOA in the thermodenuder. It solves two differential equations, for the particle and gas phase, for each one of the 4 surrogate species using the Clausius-Clapeyron equation for the change of the saturation vapor pressure as a function of temperature. The input to this model is the initial partitioning of the 4 species of different volatility that have been calculated from the smog chamber model. The output is the mass fractions of the 4 species at the exit of the thermodenuder (Figures 2.1, 2.2 and 2.3). The thermodenuder model is described in detail in Lee et al. (2010) and its predicted VFR has been shown to reproduce the measured VFR by the SMPS quite well. The model suggests that in the smog chamber (depending on the experiment) the SOA has contributions from all four VBS surrogate species. As the temperature in the thermodenuder increases the concentration of the 100 and 1000 $\mu\text{g m}^{-3}$ surrogate species in the aerosol phase approaches zero and the SOA exiting the thermodenuder is dominated by the 1 and 10 $\mu\text{g m}^{-3}$ components (Figure 2.1).

Figure 2.1: Predicted composition of α -pinene SOA after passing through the thermodenuder as a function of the temperature: a) for low NO_x , low RH conditions and b) for high NO_x , low RH conditions.

Figure 2.2: Predicted composition of α -pinene aerosol after passing through the thermodenuder as a function of the temperature for low NO_x , 50% RH.

Figure 2.3: Predicted composition of SOA after passing through the thermodenuder as a function of the temperature: a) for limonene for low NO_x, low RH conditions, b) for limonene for high NO_x, low RH and c) for β-pinene for low NO_x, low RH conditions.

2.3.3 AMS Spectrum Deconvolution

The normalized measured AMS mass spectrum, $\mathbf{MS}(T_j)$ expressed as a vector of 300 components at temperature T_j , is deconvoluted in 3 basis mass spectra according to their volatility. We estimate the optimum solution by minimizing the error expressed as the sum of the absolute differences between the measured and the following predicted spectrum:

$$\mathbf{MS}'(T_j) = \xi_{1,T_j} \mathbf{MS}_1 + \xi_{2,T_j} \mathbf{MS}_{10} + (\xi_{3,T_j} + \xi_{4,T_j}) \mathbf{MS}_{100-1000} \quad [2.1]$$

where T_j is the temperature in the thermodenuder for the j th measurement, $\mathbf{MS}'(T_j)$ is the reconstructed AMS mass spectrum considered as a vector of 300 components at temperature T_j , ξ_{i,T_j} is the estimated, by the above models, mass fractions of each volatility basis-set component at temperature T_j in the exit of the thermodenuder and $\mathbf{MS}_1, \mathbf{MS}_{10}, \mathbf{MS}_{100-1000}$ are the unknown mass spectra vectors for each component. The two species of higher volatility (100 and 1000 $\mu\text{g m}^{-3}$) are treated as one and their mass fraction is the sum of their contributions. The reason for this choice is the low mass fraction of the 1000 $\mu\text{g m}^{-3}$ surrogate species (Figure 2.1), and thus the limited information about the individual higher volatility species in all experiments. To calculate the uncertainty of the estimated spectra we also find the solutions that give an error within $\pm 20\%$ of the minimum. These solutions are represented with error bars at each m/z .

Angle θ . The coefficient of determination R^2 has been often used as a measure of the agreement between two AMS mass spectra. In this work for the comparison of two AMS

mass spectra we use the angle θ between the corresponding vectors. The AMS mass spectra, $\mathbf{MS}_A$ and $\mathbf{MS}_B$, can be written as vectors with 300 dimensions:

$$\mathbf{MS}_A = \alpha_1 \mathbf{m/z}_1 + \alpha_2 \mathbf{m/z}_2 + \cdots + \alpha_{300} \mathbf{m/z}_{300} \quad [2.2]$$

$$\mathbf{MS}_B = \beta_1 \mathbf{m/z}_1 + \beta_2 \mathbf{m/z}_2 + \cdots + \beta_{300} \mathbf{m/z}_{300} \quad [2.3]$$

where $\mathbf{m/z}_1, \mathbf{m/z}_2 \cdots \mathbf{m/z}_{300}$ are the dimensions corresponding to the m/z channels of AMS and $\alpha_1, \alpha_2, \dots, \alpha_{300}$ and $\beta_1, \beta_2, \dots, \beta_{300}$ are the values of the corresponding m/z channel in the spectra A and B. The angle θ between the two vectors is given by:

$$\cos(\theta) = \frac{\mathbf{MS}_A \mathbf{MS}_B}{|\mathbf{MS}_A| |\mathbf{MS}_B|} \quad [2.4]$$

where $\mathbf{MS}_A$ and $\mathbf{MS}_B$ are the two AMS mass spectra. The correlation coefficient R is equal to the cosine of the angle θ that we will use in this work for mass spectra comparison.

2.4 Results and Discussion

2.4.1 Mass Fraction Remaining

The mass fraction remaining (MFR) is the ratio of the SOA mass concentration after the thermodenuder to the mass concentration in the smog chamber based on the AMS measurements. The MFR provided by the AMS was in good agreement with the volume fraction remaining (VFR) measured by the SMPS for all experiments having a correlation coefficient $R^2=0.983$ (Figure 2.4). There is a small tendency of the AMS to produce higher remaining mass fractions than the SMPS, but it is within experimental error most of the time. Potential reasons for this small bias include a small change in shape or density of the particles during heating, change in the collection efficiency of the

AMS for the thermodenuded SOA, etc. The behavior of the SOA mass according to the AMS is consistent with the volume measurements by the SMPS discussed and analyzed by Lee et al. (2010) and will not be discussed further here.

Figure 2.4: Comparison between MFR from the AMS and VFR from the SMPS for all the experiments.

2.4.2 Changes in Mass Spectra during the Experiments

In each experiment we compared the mass spectra of the SOA in the smog chamber after the mass concentration had reached the maximum value to those at the end of the experiment (4-5 hours later) and found them to be alike in all cases (θ was 2-3 degrees). This denotes that the chemical composition of the SOA after its formation did not change appreciably after 4-5 hours of exposure to high levels of ozone.

We compared the AMS mass spectra of the smog chamber SOA to the mass spectra of the thermodenuded SOA (for the same precursor and conditions) calculating the angle

θ between them using equation [2.4] (Figure 2.5). For the less volatile SOA fraction (MFR<0.1) the θ exceeded 10 degrees for the monoterpenes suggesting differences in composition for species of different volatilities. The β -caryophyllene SOA showed much less variation with θ less than 6 degrees even for MFR<0.05.

2.4.3 Mass Fragment Behavior

The trend of the SOA fragments for m/z 's 44 and 43 with SOA volatility was investigated first. In all conditions and for all precursors the m/z 44 increases at lower SOA concentrations (as the temperature in the thermodenuder increases and the mass fraction remaining decreases, Figure 2.6). For example for experiment 1 the signal fraction of the m/z 44 of the α -pinene SOA (ambient temperature, $24.5 \mu\text{g m}^{-3}$ SOA) was 7.2%, but when 80% of the SOA evaporated ($T=64^\circ\text{C}$, $5.7 \mu\text{g m}^{-3}$ SOA) the signal fraction of the m/z 44 for the remaining aerosol increased to 9.9%, resulting in a 37.5% increase of the m/z 44. All the monoterpene SOA followed the same trend and the percentage increase of the m/z 44 ranged from 11-38%. These results are consistent with the work of Shilling et al. (2009) for α -pinene SOA, who also reported that the signal fraction of the m/z 44 increased as the SOA particle mass loading decreased. For β -caryophyllene SOA the m/z 44 also increased as the MFR decreased (10% for experiment 10 and 25% for experiment 11). This indicates that the concentration of CO_2^+ (m/z 44) is higher for the less volatile SOA. As a result, the lower volatility SOA components that will dominate ambient concentrations are more oxygenated than the average SOA investigated in typical smog chamber experiments.

Figure 2.5: Mass spectra comparison between smog chamber and thermodenuded SOA a) for α -pinene, b) for β -pinene, c) for limonene and d) for β -caryophyllene, expressed as the θ between versus the MFR. By definition for MFR 1 (ambient temperature in the thermodenuder) the θ should be 0. In our experiments the θ is higher (0.48-3.7 degrees) and this difference is probably noise.

Figure 2.6: Mass fraction of fragments m/z 44 versus MFR in the thermodenuder for 100 ppb precursor and at low NO_x , RH conditions i.e. experiments 1 (α -pinene), 12 (β -pinene), 5 (limonene) and 10 (β -caryophyllene). The less volatile SOA is more oxygenated.

For limonene and β -caryophyllene SOA the signal fraction of m/z 43 decreases 20-30% as the MFR and therefore the volatility decreases (Figure 2.7a). A different behavior of m/z 43 was observed for β -pinene, where it generally showed an increasing trend as the volatility decreased, while in low NO_x experiments it remained practically constant up to 60-70°C (MFR: 0.3-0.1) and then decreased as the volatility decreased. For α -pinene the m/z 43 generally has a decreasing trend as the volatility decreases except for high NO_x

conditions where it decreased up to 40°C (MFR=0.7), then increased sharply up to 50°C (MFR=0.3) and then again decreased reaching a lower point relatively to the initial value.

The ratio of m/z 43 over m/z 44 for α -pinene experiments is shown in Figure 2.7b. For high NO_x concentrations this ratio was 1.2–3.5 times higher than in low NO_x conditions for all precursors. This suggests that in high NO_x conditions the SOA is less oxidized than in low NO_x conditions. This behavior is expected as organic nitrate compounds formed under high NO_x levels are typically more volatile and less oxidized than the species formed at low NO_x conditions (Presto et al., 2005; Duplissy et al., 2008). For 50% RH, the ratio of m/z 43 over m/z 44 was in the same range as that for the low RH conditions for α - and β -pinene. This indicates that RH for α - and β -pinene has a small affect on the degree of oxidation of SOA. This is consistent with the conclusion of Lee et al. (2010), that the RH did not affect significantly the volatility of the α - and β -pinene SOA products. However, for limonene for 50% RH this ratio was 1.5-1.7 times lower suggesting that the limonene products contain more oxidized components at medium than at low RH.

2.4.4 Deconvolution and Reconstruction of Mass Spectra

Using the 2 models described above we calculated the mass fraction of the 4-species for our α -pinene, β -pinene and limonene experiments (Figure 2.1). There are no data available for basis-set fits for β -caryophyllene, for limonene at 50% RH and for β -pinene at 50% RH and at high NO_x conditions and therefore these cases were not analyzed further.

For low NO_x, low RH conditions (Figure 2.1a) the 1 µg m⁻³ surrogate species represents approximately 30% of the α-pinene SOA at ambient temperatures and dominates the SOA composition when the TD temperature exceeded 60°C. Its concentration exceeded that of the 10 µg m⁻³ species for all temperatures. Limonene and β-pinene experiments (Figures 2.3a and 2.3c) in the same low NO_x, low RH conditions showed the same behavior as α-pinene. In low NO_x, medium RH conditions for α-pinene (Figure 2.2) the contribution of the 10 µg m⁻³ species is significant (10-50%), but the 1 µg m⁻³ species is again dominant (10-85%) at higher temperatures. Under high NO_x conditions (Figure 2.1b) the dominant α-pinene SOA species for most temperatures is the one with C* = 10 µg m⁻³ (25-70%). At high NO_x conditions a significant fraction of the SOA consists of organonitrate species that are more volatile than the species produced under low NO_x conditions (Presto et al., 2005). In contrast, in the limonene case (Figure 2.3b) at high NO_x, low RH conditions the contribution of the 1 µg m⁻³ species (15-90%) exceeds that of the 10 µg m⁻³ one (10-50%), but the second is more abundant in high NO_x than in low NO_x conditions. This lower volatility distribution of limonene SOA at high NO_x is consistent with the results of Zhang et al. (2006). These authors concluded that at low NO_x heterogeneous oxidation of the limonene the terminal double bond follows almost immediately the initial reaction of the endocyclic double bond. For high NO_x, the heterogeneous reaction is inhibited and the gas-phase oxidation of the double bond dominates yielding products of lower volatility.

Figure 2.7: a) Mass fraction of fragments m/z 43 versus MFR in the thermodenuder for 100 ppb precursor and at low NO_x , RH conditions i.e. experiments 1 (α -pinene), 12 (β -pinene), 5 (limonene) and 10 (β -caryophyllene). The signal fraction of m/z 43 is decreasing as the volatility decreases. For β -pinene case it slightly increases up to 60°C and then it decreases. b) Ratios of m/z 43 over m/z 44 for α -pinene cases in different conditions. The highest ratio is calculated for high NO_x conditions and this behavior is observed for all 4 precursors.

Using the calculated mass fraction of the 4-species in equation [2.1] we estimated the 3 basis mass spectra for each individual experiment. The angle θ between the reconstructed and the measured mass spectra at the same temperature was less than 10 degrees (correlation coefficient around 0.99) in all cases (Figure 2.8).

The α -pinene SOA mass spectrum of the species $1 \mu\text{g m}^{-3}$ showed a higher signal of m/z 44 than of 43 in the low NO_x cases (Figure 2.9b and Figure 2.10). The m/z 44 signal was also higher than that of 43 for the basis mass spectra of the lowest volatility surrogate species in the β -pinene SOA mass spectrum (Figure 2.9a). For the limonene SOA however even the mass spectrum of the lowest volatility component was dominated by the m/z 43 fragment (Figure 2.9c). The calculated mass spectra of the higher volatility species and the high NO_x α -pinene had a higher m/z 43 than m/z 44 signal in all cases (e.g. Figure 2.11).

Figure 2.8: Comparison of the measured and predicted (reconstructed) thermodenuded mass spectrum for experiment 3 (100 ppb α -pinene, 1040 ppb O_3 , $\text{NO}_x < 2\%$, 53% RH) at temperature 75°C .

Figure 2.9: The basis mass spectra for the surrogate species $1 \mu\text{g m}^{-3}$: a) for β -pinene (experiment 12), b) for α -pinene (experiment 1), and c) for limonene (using experiments 5, 6, 8 and 9) SOA products and d) is the mass spectra of Pittsburgh OOA as deconvoluted by Zhang et al.

Figure 2.10: The basis mass spectra of the surrogate species $1 \mu\text{g m}^{-3}$ for α -pinene SOA products in low NO_x , 50% RH conditions (experiment 3).

Figure 2.11: The basis mass spectra of the surrogate species 10 (a) and 100-1000 $\mu\text{g m}^{-3}$ (b) for β -pinene SOA products (using experiment 12).

The angle θ between the mass spectra of the $1 \mu\text{g m}^{-3}$ α -pinene SOA surrogate species was on average 16 degrees indicating some similarity, but also some differences especially between low NO_x and high NO_x conditions. The average θ between the $10 \mu\text{g m}^{-3}$ and $100\text{-}1000 \mu\text{g m}^{-3}$ α -pinene SOA species for different conditions was 22.5 and 15.9 degrees correspondingly (Table 2.2). For the limonene SOA mass spectra the average angles θ at different conditions for the species 1, 10 and $100\text{-}1000 \mu\text{g m}^{-3}$ species were 9.9, 12.7 and 6.7 degrees (Table 2.2). With the exception of the θ between the $10 \mu\text{g m}^{-3}$ α -pinene SOA species (22.5 degrees) the mass spectra of the 3 species derived from the individual experiments are relatively similar to each other. These relatively modest differences of the mass spectra of the SOA from the same precursor at different NO_x and RH conditions, allow to a first approximation, the calculation and use of average spectra for all conditions. These average spectra for the surrogate species of 10 and $100\text{-}1000 \mu\text{g m}^{-3}$ for α -pinene and limonene SOA are shown in the Figures 2.12 and 2.13. The main difference between α -pinene and limonene SOA products is the much higher signal in m/z 43 in all basis mass spectra for limonene.

The calculated mass spectra can be used together with the model results about the volatility distribution of the SOA to reproduce the variation of m/z 44 with the mass fraction remaining (shown in Figure 2.6) and m/z 43 (shown in Figure 2.7a). The results of this comparison are shown in Figure 2.14.

The angle θ between the average mass spectrum of SOA of each precursor and the mass spectra of OOA and HOA, deconvoluted by Zhang et al. (2005), was estimated. These overall SOA mass spectra did not compare well nor with the ambient OOA (θ between 32-42 degrees) nor with the HOA (θ between 38 and 45 degrees). However, the

individual spectra of the lower volatility components ($1 \mu\text{g m}^{-3}$ saturation concentration) for α - and β -pinene are a lot more similar to OOA, giving angles 10-20 degrees (Figure 2.9). This is consistent with other recent studies (Shilling et al., 2009; Duplissy et al., 2008). On the contrary none of the 3 limonene basis mass spectra of each experiment are similar to the OOA (θ between 30 and 50 degrees).

Table 2.2: Comparison of the angle θ between the mass spectra of the same surrogate species for the same precursor and at different conditions. Note that for β -pinene only the mass spectra at low NO_x , low RH conditions are available.

Mass spectra of surrogate species	Angle θ
$1 \mu\text{g m}^{-3}$ α -pinene SOA	16
$10 \mu\text{g m}^{-3}$ α -pinene SOA	22.5
$100\text{-}1000 \mu\text{g m}^{-3}$ α -pinene SOA	15.9
$1 \mu\text{g m}^{-3}$ limonene SOA	9.9
$10 \mu\text{g m}^{-3}$ limonene SOA	12.7
$100\text{-}1000 \mu\text{g m}^{-3}$ limonene SOA	6.7

Figure 2.12: The basis mass spectra of the surrogate species 10 (a) and 100-1000 $\mu\text{g m}^{-3}$ (b) for α -pinene SOA products (using experiments 1, 2, 3 and 4).

Figure 2.13: The basis mass spectra of the surrogate species 10 (a) and $100-1000 \mu\text{g m}^{-3}$ (b) for limonene SOA products (using experiments 5, 6, 8 and 9).

Figure 2.14: Comparison of the reproduced spectra (dotted lines) with the measurements (solid lines) for the signal fraction of m/z 43 (a) and 44 (b) for the low NO_x low RH experiments. The reconstructed spectra can reproduce the major features of the observed behavior.

2.4.5 Sensitivity Study

We recalculated the basis mass spectra for all cases correcting the mass spectra for m/z 28 (CO^+) and also for 16, 17, 18, 19 and 20 (water) changing the fragment table according to the suggestions of Aiken et al. (2008). We then estimated a new OOA mass spectrum applying the Aiken et al. (2008) corrections to OOA mass spectra of Zhang et al. (2005). The comparison between the new OOA mass spectra and the new basis mass spectra resulted in the same range of θ .

The base-case choice using the 3 general basis mass spectra, choice A, (1, 10 and 100-1000 $\mu\text{g m}^{-3}$) was compared to alternative mass spectra combinations using just 2 basis mass spectra. We tried three combinations: B (1-10, 100-1000 $\mu\text{g m}^{-3}$), C (1, 10-100-1000 $\mu\text{g m}^{-3}$) and D (1-10-100, 1000 $\mu\text{g m}^{-3}$). Our combination A gives the optimum reconstructed mass spectra resulting in an average θ of 6.8 degrees when applied to each individual experiment, while choice C is second best giving an average θ of 8.3 degrees. The standard deviation for case A was also lower (± 3.5 degrees) than for case C (± 4.6 degrees). Choices B and D had even worse performance.

2.5 Conclusions

The SOA AMS mass spectra can be deconvoluted to individual spectra of the volatility basis set surrogate species. The less volatile α - and β -pinene SOA components are quite similar to OOA and this is consistent with other recent work (Shilling et al., 2009; Duplissy et al., 2008), while the overall SOA mass spectra are not. Ambient SOA is dominated under most conditions by components of lower volatility and that part of the discrepancy between laboratory and field AMS mass spectrum is due to the difference in

SOA composition with volatility. This analysis in combination with the volatility basis-set could be the base for predicting the AMS mass spectra, as a function of space and time by a chemical transport model.

The AMS spectrum obtained after passing the SOA through the thermodenuder and reducing its concentration to say $1 \mu\text{g m}^{-3}$ is, in general, different from that of a low concentration SOA experiment that produced at ambient temperature the same SOA concentration of $1 \mu\text{g m}^{-3}$. The difference is the temperature. The SOA produced in the low concentration experiment at ambient temperature will have higher contributions from the higher volatility components compared to the thermodenuded SOA. So thermodenuding the SOA and reducing progressively its concentration is not equivalent to performing the experiment at the corresponding concentration level. This is exactly where the proposed deconvolution approach becomes useful, because it can separate the spectra at higher temperatures and concentrations and bridge the gap between the two types of experiments and results. The use of medium concentrations in these experiments is actually beneficial because it allows us to span a wide range of concentrations (high at ambient temperature and low at high TD temperature) and thus obtain information of the mass spectra of most surrogate species. Experiments at even higher concentrations than used here are necessary to obtain the mass spectrum of the $1000 \mu\text{g m}^{-3}$ volatility bin.

2.6 References

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Chapter 3

An Algorithm for the Calculation of Secondary Organic Aerosol Density Combining AMS and SMPS Data

This work has been published as:

Kostenidou, E., Pathak, R. K., and Pandis, S. N. (2007). An algorithm for the calculation of secondary organic aerosol density combining AMS and SMPS data, *Aerosol Science and Technology*, 41, 1002-1010.

3.1 Introduction

Atmospheric aerosols play an important role in atmospheric chemistry and global climate change (IPCC, 2001) affecting human health, air quality, and visibility (Seinfeld and Pandis, 2006). Atmospheric particles mainly consist of sulfates, nitrates, ammonium, dust, water, metals and organic matter. A significant fraction of their mass in both rural and urban areas is formed from gas-to-particle conversion (secondary aerosol).

SOA may be produced by either anthropogenic or biogenic precursors. Emissions of biogenic volatile organic compounds (VOCs) exceed anthropogenic on both continental and global scales (Rasmussen, 1972; Zimmerman et al., 1978; Guenther et al., 1995). Monoterpenes represent about 10% to 50% of the biogenic non-methane hydrocarbon emissions (Lamb et al., 1987; Müller, 1992; Guenther et al., 1995). These compounds are highly reactive and can be oxidized by ozone, NO₃ and OH radicals (Atkinson, 1997; Jang and Kamens, 1999; Yu et al., 1998; Glasius et al., 1997, 1999a, b, 2000; Koch et al., 2000; Jaoui and Kamens, 2001; Kamens and Jaoui, 2001). Monoterpenes may contribute as much as 50% to the total organic aerosol (Andersson-Sköld and Simpson, 2001). In the US roughly half of the monoterpene emission is α -pinene, β -pinene and d-limonene (Lamb et al., 1993). Our knowledge of SOA's chemical and physical properties (e.g. density) is however limited.

Elemental carbon (EC) has a density of approximately 2 g cm⁻³ (Seinfeld and Pandis, 2006). For organic aerosol the values that are often used are 1-1.2 g cm⁻³ (Odum et al., 1997; Hoffman et al., 1997; Turpin and Lim, 2001; McMurry et al., 2002; Presto et al., 2005; Pathak et al., 2006). However, densities of compounds that have been detected in aerosol particles in the cyclohexene-ozone system, e.g. adipic acid, glutaric acid and

oxalic acid (Kalberer et al., 2000; Ziemann, 2002; Ziemann, 2003) range from 1.36 to 1.9 g cm⁻³ (Table 3.1). The boiling point for these compounds is usually higher than 35°C, so at room temperature most of them are solid. However, for the densities of the monoterpene major SOA products there is little available information.

Several techniques for measuring aerosol density have been developed. The density provided by aerosol mobility-based techniques includes the effects of potential voids in the particles and is usually called effective density. For spherical particles without voids the effective density is equal to the inherent material density. Hänel and Thudium (1977) estimated the density of bulk dry atmospheric aerosol samples measuring independently their mass and volume. For the volume measurements a specially designed gas pycnometer was used but the measurement accuracy was low. Kousaka et al. (1981) inferred the density of spherical aerosol particles using direct measurements of their mass (using a piezo-electric mass monitor) and their volume by integration of the size distributions provided by a differential mobility analyzer (DMA). Kelly and McMurry (1992) developed a technique for density measurements combining a DMA and an impactor. This method was applied by Stein et al. (1994) for atmospheric particles in Meadview, Arizona resulting in densities in the range 1.60 – 1.79 g cm⁻³. Another approach for calculating particle density developed by McMurry et al. (2002) involves a DMA and the Aerosol Particle Mass analyzer by Ehara. This technique was applied to urban atmospheric aerosols in Atlanta, Georgia, and the calculated density fell in the range of 1.54 to 1.77 g cm⁻³. Khlystov et al. (2004) developed an algorithm to combine size distributions measured by an SMPS and an Aerodynamic Particle Sizer. The

algorithm was tested with ambient aerosols in the Pittsburgh Air Quality Study resulting in an effective density of $1.5 \pm 0.3 \text{ g cm}^{-3}$.

Alfarra et al. (2006) determined an effective density of around 1.3 g cm^{-3} for trimethylbenzene and α -pinene SOA combining selected particle mobility diameters estimated by a DMA and the corresponding vacuum aerodynamic diameters measured by the AMS. The effective density of SOA from oxidation of cycloalkenes, terpenes and m-xylene was estimated around 1.1 g cm^{-3} for seeded experiments and around 1.4 g cm^{-3} for unseeded experiments (Bahreini et al., 2005) comparing the volume concentration measured by an SMPS and the mass concentration provided by the AMS. In this method the effective density was estimated by matching the AMS and the corresponding SMPS volume distributions. However, this approach relies on the critical assumption that the particle density is constant for all sizes. The same method gave an average SOA density of 1.3 g cm^{-3} for monoterpene and oxygenated terpene precursors in seeded experiments (Varutbangkul et al., 2006).

Despite the recent progress there is still no general method for the calculation of the density of organic particulate matter in rapidly varying organic-inorganic aerosol systems with size-dependent composition. In this study we extend the Bahreini et al. (2005) approach by relaxing the assumption of constant particle density with size. Performance of SOA experiments at low (close to ambient) levels requires inorganic seeds (Pathak et al., 2006) therefore this approach can be used for the SOA characterization under conditions closer to these of the ambient atmosphere.

Table 3.1: Densities of selected organic compounds.

Compound	Chemical Formula	Physical Properties	Density (g cm ⁻³)
Ascaridole	C ₁₀ H ₁₆ O ₂	Liquid	1.01
(+)-Camphoric acid	C ₉ H ₁₆ O ₄	Solid	1.19
trans-Cinnamic acid	C ₆ H ₈ O ₂	Solid	1.25
Anthraquinone	C ₁₄ H ₈ O ₂	Solid	1.42
Phloroglucinol	C ₆ H ₆ O ₃	Solid	1.46
1,2-Acenaphthylenedione	C ₁₂ H ₆ O ₂	Solid	1.48
adipic acid ^a	C ₆ H ₁₀ O ₄	Solid	1.36
glutaric acid ^a	C ₅ H ₈ O ₄	Solid	1.42
malonic acid ^a	C ₃ H ₄ O ₄	Solid	1.62
oxalic acid ^a	C ₂ H ₂ O ₄	Solid	1.90
succinic acid ^a	C ₄ H ₅ O ₄	Solid	1.57

(Source: CRC Handbook of Chemistry and Physics 87th Edition, 2006)

^aCompounds found in aerosol particles after cyclohexene ozonolysis (Kalberer et al., 2000; Ziemann, 2002; Ziemann, 2003).

3.2 Experimental Approach

α -pinene, β -pinene and limonene ozonolysis experiments (Tables 3.2 and 3.3) were carried out in the Carnegie Mellon University smog chamber (Figure 3.1). SOA compounds formed in these systems include pinic acid, pinonaldehyde, pinonic acid and nopinine (Jang et al., 1998; Jang et al., 1999). Each experiment lasted 6-9 h. The number size distribution of the particles was measured by an SMPS (TSI model 3936) and their mass distribution by an AMS (Aerodyne). The volume size distribution was then determined from the SMPS measurements assuming spherical particles.

Smog Chamber: All experiments were conducted in a 10 m³ Teflon reactor (Welch Fluorocarbons). The reactor was first filled with clean air, containing less than 1 cm⁻³ particles and 2-butanol (0.5ml, Sigma Aldrich, purity 99.5%) as OH-scavenger. For seeded experiments ammonium sulfate particles were generated by an Atomizer (TSI model 3076) using an aqueous ammonium sulfate (0.9 g L⁻¹) solution. The atomized ammonium sulfate was dried using a silica gel dryer. Then the SOA precursors, α -pinene, β -pinene, or d-limonene (Sigma Aldrich, purity 99.9 %) were injected. The hydrocarbon was reacted with ozone produced by an ozone generator (Azco HTU500ACPS) and measured by a continuous ozone analyzer. The temperature was kept constant during each experiment and ranged from 15 to 40°C. The relative humidity was less than 10% in all experiments.

SMPS: The SMPS system (TSI model 3936) operated at a sheath flow rate of 5 L min⁻¹ while the sample flow rate was 1 L min⁻¹. This system provided the number size

distribution and assuming spherical particles the volume size distribution versus the mobility diameter (D_m) in the range of 10-500 nm can be determined.

AMS: An AMS (Jayne et al., 2000; Jimenez et al., 2003; Allan et al., 2003; Alfarra et al., 2004; Canagaratna et al., 2006) was used to measure the chemical composition, mass concentration and also mass size distribution of the SOA versus the vacuum aerodynamic diameter (D_{va}).

The mass distributions calculated from the AMS are in the range of 80-1000 nm (in D_{va}), while the volume distributions measured by the SMPS are in the range of 60-600 nm (in D_m). As a result the AMS fully covers the distributions provided by the SMPS for these experiments.

Table 3.2: Experimental conditions and calculated SOA density for seeded experiments.

Exper. Number	Precursor	Initial Precursor Concen. (ppb)	Initial Seed Number (cm ⁻³)	Initial seed mass (µg m ⁻³)	Ozone (ppm)	Temp. (°C)	SOA Density (g cm ⁻³)	Error Score (%)
1a	α-pinene	14.4	4600	12.4	0.5	20	1.41±0.06	18
2a	β-pinene	16	6900	10.3	0.5	15	1.50±0.02	12
3a	d-limonene	6	10500	8.9	0.5	40	1.65±0.16	16
4a	d-limonene	10	10200	17.5	0.1	15	1.60±0.04	12
5a	d-limonene	6	16300	21.9	0.5	15	1.50±0.04	11
6a	d-limonene	6	15900	21.2	0.5	30	1.56±0.12	14
7a	d-limonene	30	23700	38.6	0.5	15	1.40±0.02	15
8a	d-limonene	10	11700	16.3	0.2	15	1.40±0.14	16
9a	d-limonene	3	10300	14.6	0.5	40	1.32±0.18	26
10a	β-pinene	40	2300	3.7	1.0	20	1.40±0.04	24

Table 3.3: Experimental conditions and calculated SOA density for unseeded experiments.

Experiment Number	Precursor	Initial Concentration (ppb)	Ozone (ppm)	Temp. (°C)	SOA Density (g cm ⁻³)	Error Score (%)
1b	α-pinene	20	1.50	20	1.5±0.02	34
2b	α-pinene	110	0.85	15	1.00±0.02	26
3b	α-pinene	110	0.30	20	1.5±0.02	25
4b	α-pinene	110	1.00	20	1.5±0.02	26
5b	α-pinene	14	2.00	20	1.55±0.1	33
6b	α-pinene + β-pinene	106 106	0.60	20	1.48±0.06	28
7b	β-pinene	110	1.30	20	1.5±0.04	20
8b	β-pinene	120	1.50	15	1.41±0.04	23
9b	β-pinene	16	3.00	15	1.00±0.02	44
10b	β-pinene	20	1.50	20	1.46±0.1	42
11b	d-limonene	16	0.62	15	1.57±0.1	22
12b	α-pinene	110	0.85	15	0.90±0.02	20
13b	β-pinene	16	3.00	15	0.90±0.02	50

Figure 3.1: Schematic of the experimental setup.

3.3 AMS Collection Efficiency and Relative Ionization Efficiency

The AMS does not measure all the aerosol material entering the instrument due to bounce of the less-volatile particles on the vaporizer (ion collection efficiency or ICE) and the partial transmission of particles (particle collection efficiency or PCE). The ICE is general a function of the aerosol composition and morphology. PCE depends on the size and shape of the particles. The overall collection efficiency, CE, is equal to the product of ICE and PCE.

In our experiments the diameters of the SOA particles were always in the range of 60-600 nm and assuming that they are approximately spherical the particle collection efficiency should be close to unity (Jayne et al., 2000). This assumption about the shape of the particles will be discussed in a subsequent section.

The ion collection efficiency (ICE) can be viewed as a measure of the number of ions that actually reach the AMS detector out of the total number of ions that can be produced of the particles in the instrument. The ICE depends on the ability of the particle to bounce in the AMS vaporizer. In the lab, oleic acid has an ICE of 1 (Allan et al., 2004) while citric acid has an ICE of 0.2 for dry particles and around 0.4 for aqueous (Mathew et al., 2004). The ICE of ammonium sulfate particles varies as a function of relative humidity (0.2 when dry and 1 when aqueous) but ammonium nitrate particles have ICE around 1 both at high and low RH (Mathew et al., 2004). For ambient organics particles internally mixed with sulfate in the accumulation mode ICE appears to be close to 0.5 (Zhang et al., 2005). Despite these efforts there are still significant uncertainties about the ICE of ambient and laboratory aerosol particles.

Relative ionization efficiency (RIE) is the ratio of the electron impact ionization efficiency of a given species to the measured ionization efficiency of nitrate on a per unit mass basis. RIE values of each species are determined using the approach of Jimenez et al. (2003) and Alfarra et al. (2004). For organics the RIE value is 1.4, for sulfate 1.2, and for nitrate 1.1 ($RIE_{\text{nitrate}} = \text{true IE of nitrate} / IE_{\text{nitrate}}$), where the true IE of nitrate is calculated from all fragments produced by nitrate and the IE_{nitrate} is estimated only from the ion fragments 30 (NO^+) and 46 (NO_2^+). For ammonium the RIE is estimated by ionization efficiency calibrations because at the relevant m/z ratios (15 for NH^+ , 16 for NH_2^+ and 17 for NH_3^+) there are significant interferences from CH_3^+ (m/z 15), O^+ (m/z 16) and OH^+ (m/z 17) (Canagaratna et al., 2006). The determination of the mass concentration of each species has been described in detail by Jimenez et al. (2003) and Canagaratna et al. (2006).

3.4 Algorithm for SOA Density Estimation

The mass and volume distribution are related by:

$$\frac{dV}{d \log D_m} = \frac{d(M / \rho)}{d \log D_m} \frac{1}{CE} \quad [3.1]$$

where ρ is the total density of the particles and CE the collection efficiency of the AMS. Assuming volume additivity in a system containing ammonium sulfate and SOA, the density ρ is given by:

$$\rho = \left[\frac{x_{a/s}}{\rho_{a/s}} + \frac{x_{SOA}}{\rho_{SOA}} \right]^{-1} \quad [3.2]$$

where $x_{a/s}$ is the mass fraction of ammonium sulfate, x_{SOA} is the mass fraction of SOA, $\rho_{a/s}$ is the density of ammonium sulfate (1.77 g cm^{-3}) and ρ_{SOA} is the unknown SOA density.

For spherical particles the relationship between the mobility diameter (D_m) and the vacuum aerodynamic diameter (D_{va}) is (DeCarlo et al. 2004):

$$D_m = \frac{D_{va}}{\rho} \rho_o \quad [3]$$

where ρ_o is the unit density (1 g cm^{-3}).

In the case of pure SOA particles $\rho = \rho_{SOA}$ and thus equations [3.1]-[3.3] give:

$$\frac{dV}{d \log D_m} = \frac{D_m}{D_{va} \rho_o} \frac{dM}{d \log D_{va}} \frac{1}{CE} \quad [4]$$

For mixed inorganic-organic particles in a smog chamber the composition is usually not constant with diameter (Figure 3.2) so the density varies with size. Organic vapor condenses mostly on the particles in the size range that has most of the surface area forming SOA. As a result in these experiments smaller particles contain more SOA than larger particles.

For this more complicated case the SOA density can be calculated by the following algorithm that relies on the estimation of a volume distribution as a function of the mobility diameter from the AMS mass distribution as a function of aerodynamic diameter:

(1) The aerodynamic diameter size range is discretized in sections (6 to 8 sections are used).

Figure 3.2: Mass distribution of the aerosol versus vacuum aerodynamic diameter in experiment 5a (6 ppb of limonene reacted with 0.5 ppm ozone at 15°C in the presence of ammonium sulfate seeds). The composition is not constant with the diameter. Larger particles contain more ammonium sulfate than smaller particles.

(2) The values of ammonium sulfate mass fraction ($x_{a/s}$) and SOA mass fraction (x_{SOA}) at the mean vacuum aerodynamic diameter of each section are then calculated using the AMS measurements.

(3) A guess for SOA density is made, for example 1 g cm^{-3} .

(4) The effective density of each section is calculated using equation [3.2].

(5) The effective density is calculated as a function of the vacuum aerodynamic diameter using a bilinear fit (Figure 3.3) of the following form:

$$\rho = e + fD_{va} \quad [3.5]$$

(6) The volume distribution as a function of the mobility diameter based on the AMS measurements is then calculated. Combining equations [3.3] and [3.5]:

$$D_{va} = \frac{eD_m}{\rho_o - fD_m} \quad [3.6]$$

Figure 3.3: Effective density (ρ) versus the mean vacuum aerodynamic diameter (D_{va}) for experiment 5a (6 ppb of limonene, 0.5 ppm ozone, and ammonium sulfate seeds). The density is calculated as a function of the vacuum aerodynamic diameter, using a bilinear fit of the form $\rho = e + fD_{va}$. The discontinuity does not create any problems in the algorithm.

Equation [3.1] can be rewritten as:

$$\frac{dV}{d \log D_m} = \left(\frac{1}{\rho} \frac{dM}{d \log D_m} + M(D_{va}) \frac{d(1/\rho)}{dD_m} \cdot D_m \cdot \ln 10 \right) \frac{1}{CE} \quad [3.7]$$

The term $\frac{dM}{d \log D_m}$ can be written as:

$$\frac{dM}{d \log D_m} = \frac{dM}{d \log D_{va}} \frac{D_m}{D_{va}} \frac{dD_{va}}{dD_m} \quad [3.8]$$

Differentiating equation [3.6] with respect to the mobility diameter (D_m) and combining with equation [3.3] gives:

$$\frac{dD_{va}}{dD_m} = \frac{\rho^2}{e\rho_o} \quad [3.9]$$

Differentiating equation [3.3] with respect to the mobility diameter (D_m) and combining with equation [3.9] gives:

$$\frac{d(1/\rho)}{dD_m} = -\frac{f}{e\rho_o} \quad [3.10]$$

Combining equations [3.7], [3.8], [3.9] and [3.10] results in the desired equation for the calculation of the AMS-based volume distribution:

$$\frac{dV}{d \log D_m} = \left(\frac{1}{e} \frac{dM}{d \log D_{va}} - M(D_{va}) \frac{f}{e} \frac{D_{va}}{\rho} \ln 10 \right) \frac{1}{CE} \quad [3.11]$$

where $M(D_{va})$ is the cumulative mass distribution function based on AMS measurements given by:

$$M(D_{va}) = \left(\int_{-\infty}^{D_{va}} \frac{dM}{d \log D_{va}} d \log D_{va} \right) \quad [3.12]$$

The above approach is repeated for different guesses of the organic aerosol density in step (3) and for various ICEs. The tested range of SOA density is 1.2-1.9 g cm⁻³ and that of the ICE is 0.1-1.0. Figure 3.4 illustrates estimated volume distributions from the AMS measurements for SOA density 1.2-1.9 g cm⁻³ assuming ICE=0.6 for this example. These are compared with the volume distribution calculated from the SMPS measurements. The value of the estimated density depends only weakly on the chosen ICE, as we will see later, but the goodness of the fit of the two distributions is quite sensitive to the ICE choice.

Figure 3.4: Volume distributions calculated from AMS measurements for SOA density 1.2-1.9 g cm⁻³ assuming ICE=0.6 and their comparison to the SMPS volume distribution. Measurements made at 45 minutes from the beginning of experiment 5a, where 6 ppb of limonene reacted with 0.5 ppm ozone in the presence of ammonium sulfate seeds.

To select the best fit and therefore the appropriate combination of SOA density and ICE we define the error score for time t :

$$Error\ Score_t = \frac{\sum_i |a_{ti} - b_{ti}|}{\sum_i |a_{ti}|} \quad [3.13]$$

where a_{ti} is the value of the SMPS volume distribution at section i (mobility diameter) for the time t and b_{ti} is the corresponding value of the volume distribution estimated from the AMS for the same section and time using [3.11]. The organic aerosol density is the one that together with the appropriate choice of ICE minimizes the error score in equation [3.13].

In cases where there appears to be no temporal change in the estimated density the information can be pooled together and the algorithm can minimize the sum of all the error scores, calculating the average density during the experiment. In this case, we

compare the volume distributions from the AMS and SMPS for around 10 periods in each experiment and an average error score (Figure 3.5) is estimated for each experiment for a choice of SOA density and ICE. A graph of the average error score as a function of SOA density and ICE is shown in Figure 3.6.

The duration of each experiment was 6-9 h. We could not detect any temporal trends in density in our experiments. Therefore the sum of all error scores was minimized. In that case the reported uncertainty corresponds to two standard deviations of the measured densities during different periods.

Figure 3.5: Error score vs SOA density for different collection efficiencies for experiment 5a (6 ppb of limonene, 0.5 ppm ozone, and ammonium sulfate seeds).

Figure 3.6: Average error score as a function of SOA density and ICE. This contour graph is for experiment 5a (6 ppb of limonene, 0.5 ppm ozone, and ammonium sulfate seeds).

3.5 Results

Volume distributions, from the SMPS, and mass distribution, provided by the AMS, of dry ammonium sulfate were compared as a first test of this approach. A density of 1.77 g cm^{-3} and an ICE of approximately 0.55 resulted in the optimum agreement between the instruments (Figure 3.7).

Figure 3.7: Comparison of SMPS and AMS volume distributions of ammonium sulfate. A density of 1.77 g cm^{-3} (which is the density of ammonium sulfate) and an ICE of approximately 0.55 results in the best agreements between the two instruments.

3.5.1 Seeded Experiments

The ratio of total ammonium sulfate to the total organic mass was higher than 0.30 except for experiments 7a and 10a, where it was less than 0.15. For α -pinene the SOA density was found to be $1.41 \pm 0.06 \text{ g cm}^{-3}$, for β -pinene $1.45 \pm 0.14 \text{ g cm}^{-3}$ and for d-limonene $1.49 \pm 0.24 \text{ g cm}^{-3}$ (Table 3.2).

In experiment 7a the aerosol size distribution was bimodal. In this case the experiment involved a high concentration of an efficient SOA precursor (d-limonene) reacting under relatively low temperature in the presence of a relatively high concentration of seed particles. The combination of conditions resulted in the system reaching its critical supersaturation for homogeneous nucleation and the formation of fresh pure organic particles. The first mode after the end of the reaction had a mass peak at 153 nm (in D_{va}) and the second a mass peak at 300 nm (in D_{va}) (Figure 3.8). The first mode was due to nucleation that occurred 10 minutes after d-limonene injection while the second mode due to condensation on the preexisting ammonium sulfate seeds. An SOA density of 1.40 g cm^{-3} was found to be suitable for both modes (the error score was 15%).

Figure 3.8: AMS and SMPS distributions for experiment 7a (30 ppb limonene, 1.5 ppm ozone). In this experiment two modes have been formed one by condensation and the other by nucleation.

The estimated density does not appear to change during the above experiments. The individual error scores of each data point calculated based on the average density did not show any trends. Our analysis covers the period after the rapid formation of SOA. SMPS and AMS comparison during the initial rapid condensation phase (around 20 min) is difficult, as high precision in timing is required to capture these fast dynamics.

Organic compounds with densities higher than 1.2 g cm^{-3} (Table 3.1) tend to be solid or waxy. The average SOA density in our seeded experiments is around 1.45 g cm^{-3} indicating that the particles are probably in a waxy state.

3.5.2 Unseeded experiments

In these experiments the particles were formed by nucleation and contained only α -pinene, β -pinene and d-limonene SOA (Table 3.3). The density of α -pinene SOA was approximately 1.5 g cm^{-3} in most experiments. Experiment 2b was the exception with an estimated density of $1.00 \pm 0.02 \text{ g cm}^{-3}$. For β -pinene SOA the density was $1.46 \pm 0.1 \text{ g cm}^{-3}$ except in experiment 9b where the density was $1.00 \pm 0.02 \text{ g cm}^{-3}$. For the limonene SOA the average density was $1.56 \pm 0.1 \text{ g cm}^{-3}$.

In experiment 2b two precursors were used with an initial injection of β -pinene followed by an injection of α -pinene after 10 min. The estimated SOA density of $1.48 \pm 0.06 \text{ g cm}^{-3}$ was consistent with the results of the single precursor experiments.

For these unseeded experiments, the calculated density remained constant with the time. There is no evidence of correlation between SOA density and the precursor's initial concentration.

Experiments 2b and 9b indicated much lower organic density and were in disagreement with the results of the other 19 experiments. These two experiments were repeated several months later (12b and 13b) and a density of 0.90 g cm^{-3} was estimated for both of them. This indicates that the α -pinene and β -pinene/ozone pure SOA at these conditions consists of particles of lower effective density. The reasons for this transition are not entirely clear and such low densities were not found for any of the ammonium sulfate/SOA systems. The AMS organic spectra of the experiments were similar, so a difference in composition cannot explain the observations. Another possible explanation is that the particles in these experiments had more void space.

The SOA density for most unseeded experiments is around 1.5 g cm^{-3} implying again that SOA is probably in a waxy state. A ‘tail’ was observed at the unseeded mass distributions measured by the AMS, while the SMPS does not measure any such big particles. For low precursor concentrations (around 20 ppb) the ‘tail’ is more pronounced and thus the error score is higher than in higher concentration experiments (around 100 ppb). In seeded experiments no ‘tail’ was present.

3.5.3 Sensitivity Tests

The estimated SOA density is not sensitive to the assumed set of mass correction values. We used IE_{nitrate} values of $2.143 \times 10^{-6} \text{ ions molecule}^{-1}$ and $1.847 \times 10^{-6} \text{ ions molecule}^{-1}$, for ion rates of mass air beam $1.10 \times 10^7 \text{ Hz}$ and $9.66 \times 10^6 \text{ Hz}$ and RIE_{ammonium} 5.17 and 4.9 instead of $6.171 \times 10^{-6} \text{ ions molecule}^{-1}$, $8.01 \times 10^6 \text{ Hz}$ and 4.97 respectively. The estimated density changed by only $\pm 0.05 \text{ g cm}^{-3}$.

For non-spherical particles a shape factor, χ , should be used in the equations that combine the mobility and the aerodynamic diameter (DeCarlo et al., 2004). We repeated the calculations for selected experiments using values of χ equal to 1.2. The use of a non-unit shape factor increases the minimum error score to 50-60% indicating that the SOA particles in our system were probably close to spherical.

3.6 Summary and Discussion

A new algorithm for organic aerosol density calculation in multicomponent systems was developed. This algorithm takes into account changes in particle composition with size and its results are robust with respect to the applied AMS mass corrections (IE_{nitrate} , ion rate of mass air beam and RIE_{ammonium} values). α -pinene, β -pinene and d-limonene ozonolysis experiments with and without seeds were carried out. The SOA density was estimated to be in the 1.4-1.65 g cm⁻³ range for practically all cases. For the pure SOA particles two exceptions of lower density (0.9-1 g cm⁻³) were observed. A possible reason for this behavior is that these particles had more void space.

The high density that was estimated suggests that the SOA is likely in a solid or waxy phase. A density of 1.4 – 1.65 g cm⁻³ for organics is consistent with ambient measurements of the overall particle density (Stein et al., 1994; Khlystov et al., 2004). This density is significantly higher than the few known densities of the known α -pinene photo-oxidation products (e.g., the density of pinic acid is 1.09 g cm⁻³).

This method is also applicable to the primary organics and to ambient particles assuming that these particles are close to spherical.

3.7 References

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Chapter 4

Measurements of the Organic Aerosol Chemical Composition during the Finokalia Aerosol Measurement Experiments - 2008/2009: Calculation of the AMS Collection Efficiency and the Organic Aerosol Density

This work is part of the following publications:

Hildebrandt, L., Engelhart, G. J., Mohr, C., Kostenidou E., Lanz, V., Bougiatioti, A., DeCarlo, P. F., Prevot, A. S. H., Baltensperger, U., Mihalopoulos, N., Donahue N. M., Pandis, S. N. (2010). Aged Organic Aerosol in the Eastern Mediterranean: The Finokalia Aerosol Measurement Experiment – 2008, *Atmospheric Chemistry and Physics*, 10, 1847-1900.

Hildebrandt, L., Kostenidou E., Lee, B.-H., Mihalopoulos, N., Worsnop, D. R., Donahue N. M., Pandis, S. N. (2010). Formation of Low-Volatility Oxygenated Organic Aerosol in the Atmosphere: Insights from the Finokalia Aerosol Measurements Experiments – 2008/2009, *Geophysical Research Letters* (in preparation).

4.1 Introduction

Fine atmospheric aerosols may have important adverse impacts on human health (Dockery et al., 1993; Davidson et al., 2005; Pope and Dockery, 2006). They can influence the cloud lifetime and formation, scatter and adsorb radiation and therefore affect climate change (IPCC, 2007) and the stratospheric ozone depletion (Solomon, 1999). Atmospheric particles mainly consist of sulfate, nitrate, ammonium, organic matter, dust, metals and water. Organic material may comprise a large fraction (20-90%), (Kanakidou et al., 2005) of the fine particle in the atmosphere. Organic aerosol is still poorly characterized due to the thousands of the compounds that it consists of and the multiple sources. Even though much progress has been made in recent years our knowledge about chemical and physical properties (e.g. density, volatility) is however limited.

The recent development of the Aerodyne AMS allows the real-time size and composition analysis of the non-refractory PM_{10} (NR- PM_{10}) aerosol particles. It has been used in many field measurements (Alfarra et al., 2004; Salcedo et al., 2005; Lanz et al., 2009) characterizing the chemical composition of urban, remote or coastal regions. It also provides useful information about the organic aerosol through the mass spectrum. However, there is a limitation in this system: the AMS does not measure all the aerosol material entering the instrument due to bounce of the less-volatile particles on the vaporizer, and the partial transmission of particles. The corrections are usually done by comparing the mass of inorganic species (e.g. sulfate) from a semi-continuous system such as the PILS or filters (Drewnick et al., 2004; Högrefe et al., 2004; Takegawa et al., 2005) or they assume a CE of 0.5 (Alfarra et al., 2004; Zhang et al., 2005). In this work

we extend the method of Kostenidou et al. (2007), as described in Chapter 3, to estimate the CE for field measurements.

The use of a thermodenuder for atmospheric aerosol volatility measurements has been around for over four decades. Many thermodenuders have been designed and constructed based upon the ideas of Burtscher et al. (2001) and Wehner et al. (2002) but their characteristics can vary from each other. For example, the residence time in the heated zone of can vary from 0.6 s (Jonsson et al., 2007) to 60 s (Lee et al., 2010a). Lee et al. (2010a) used an aerosol dynamics model, which is based on the volatility basis set approach (Donahue et al., 2006) and SOA yield parameters derived from smog chamber studies, to show that due to these resistances in the particulate phase or at the interface, an effective accommodation coefficient of 0.05 is needed for the description of the beginning part of the evaporation. With this set-up one can calculate the volatility of the organic aerosol and this procedure requires use of mass transfer models that can account for the effects of size, concentration, mass transfer resistances, etc.

The Finokalia Station is located at a remote site Northeast of Crete at Greece. The site is far away from local sources (Mihalopoulos et al., 1997; Kolouri et al., 2008) allowing the study of aged organic aerosol originating from different region sources. The chemical composition of the $PM_{1.3}$ and $PM_{10-1.3}$ particles at Finokalia have been characterized with 1 to 3 day time-resolution over a 2-year period from July 2004 to July 2006 (Koulouri et al., 2008). During the summer the contribution of inorganic salts to $PM_{1.3}$ can be up to 60% and the organics to 30% with a small contribution of water dust and elemental carbon. The dominant inorganic compound was found to be ammonium sulfate and ammonium bisulfate. The wind direction at Finokalia can be from Europe, Africa, Athens, Asia Minor or of marine origin. Since Finokalia is not affected by local

anthropogenic sources, it is an ideal location for studying aged organic aerosols from Europe, fresher from Athens and Asia Minor, African dust and marine aerosol.

We performed two field campaigns at the Finokalia site: FAME-08 was in the early summer (8 May to 5 June of 2008) and FAME-09 was in the winter (25 February to 25 March of 2009). We measured the size-resolved chemical composition of NR-PM₁ at high time resolution and studied the organic aerosol mass spectrum. In this study combining measurements from an AMS, an SMPS and a thermodenuder we calculated the CE of the AMS and the organic density of the ambient and the thermodenuded particles. These calculations are crucial for estimating the ambient aerosol concentration from the AMS measurements and for the estimation of the organic aerosol volatility (Chapter 5).

4.2 The Field Station of Finokalia

The measurements took place at the European Supersite for Atmospheric Aerosol Research (EUSAAR) Finokalia Station of the Environmental Chemical Processes Laboratory of the University of Crete. The station is located at a remote coastal site in the northeast of Crete, Greece, in the Eastern Mediterranean (35°20'N, 25°40'E). It is located about 70 km northeast of Heraklion, and 400 km southwest of Athens, the closest megacity. The site is far from local sources (the closest 10-people village is at a distance of 3 km) allowing the study of aged organic aerosol originating from different source regions. Further information about the Finokalia station can be found elsewhere (Mihalopoulos et al., 1997, Sciare et al., 2003).

4.3 Experimental

4.3.1 Instrumentation and Methods

A Quadrupole Aerosol Mass Spectrometer (Q-AMS or AMS, Aerodyne Research, Inc) (Jayne et al., 2000; Jimenez et al., 2003; Canagaratna et al., 2007) was employed to measure the size-resolved chemical composition of the aerosol. A scanning mobility particle sizer (SMPS, TSI model 3034 in FAME-08 and model 3030 in FAME-09) provided the number size distribution. A thermodenuder (An et al., 2007) was used for measurements of the OA volatility. 24 hours PM₁ filter samples provided a separate measure of the concentration of inorganic and organic aerosol. For FAME-08 only, a steam sampler (Khlystov et al., 1995) provided of the concentration of inorganic aerosol. The aerosol in both campaigns was sampled at ambient relative humidity to avoid the potential for other changes in the aerosol upon drying, such as evaporation of nitrate or changes in the aerosol morphology or physical state.

4.3.2 Q-AMS

The Q-AMS was operated alternating continuously between its Mass Spectrum and Time-Of-Flight modes every fifteen seconds. The sample averaging time was three minutes, and more averaging was applied in the post-analysis of the data. The vaporizer temperature was set at 600°C during FAME-08 to ensure fast and complete vaporization of the ammonium sulfate. During FAME-09 the vaporizer temperature was set to 700°C. The AMS measures only non-refractory (NR) PM₁, but it does not measure refractory material such as black carbon, sea-salt and silica. Previous studies at Finokalia (Koulouri et al., 2008), but also filter measurements during the FAME campaigns (Pikridas et al.,

2010) showed that almost 90% of the fine particle mass is non-refractory so the AMS measures most of the PM_{10} mass.

The AMS can provide three separate characteristics of the NR- PM_{10} : its chemical composition, the organic mass spectrum and the aerosol mass size distribution versus the vacuum aerodynamic diameter (Canagaratna et al., 2007).

4.3.3 Thermodenuder

A thermodenuder system based on the design described by An et al. (2007) was employed for the measurement of the volatility of the organic aerosol. The aerosol passes alternately through the thermodenuder or a bypass line. Two 3-way valves are used to control the aerosol flow direction. In order to avoid recondensation of the organic vapors activated charcoal is used in the cooling stage to absorb the organic vapors. Then the line splits in two parts: one to the AMS for real-time measurement of the aerosol chemical composition and a second one to SMPS for measurement of the online particle size distribution. The volatility is then determined by comparing the residual aerosol volume after the thermodenuder to the aerosol volume that was passed through the bypass (Lee et al., 2010). The volatility analysis will be discussed in the Chapter 5. In this chapter we will focus on the effect of aerosol heating and evaporation on the collection efficiency (CE) of the AMS and the organic aerosol density.

4.3.4 The Steam Sampler

A steam sampler coupled with an ion chromatograph provided $PM_{2.5}$ semi-continuous measurements of water-soluble inorganic ions. The system consisted of three parts: (1) a set of coated annular diffusion denuders (URG) to remove water soluble

gaseous species (e.g. NH_3 , SO_2 , HNO_3 , HCl), (2) a steam-jet aerosol collector (Khlystov et al., 1995), and (3) two ion chromatographs for anions and cations, (Metrohm 761 Compact IC) for quantitative mass analysis. The cations and anions ICs were using 1000 μl and 200 μl sample loops, respectively. As an internal standard a lithium fluoride solution of known concentration was used and mixed continuously with the sample at a flow of 0.1 ml min^{-1} .

4.4 Results and Discussion

4.4.1 Collection Efficiency and Organic Density

The AMS does not always measure the whole aerosol material entering the instrument due to bounce of less “sticky” particles on the vaporizer, the partial transmission of particles and the shape-related losses at the vaporizer (Canagaratna et al., 2006). Thus the CE is a function of the aerosol composition, morphology, shape and size. After partial evaporation of particles in the thermodenuder the CE values may also change. This is probably because of changes in particle morphology, shape or different behaviour of particles with less-volatile species on the AMS heater, or a combination of the above. The organic aerosol density may also change after heating through the thermodenuder.

We calculated the organic density and the CE of the AMS for both ambient and thermodenuded aerosol using the algorithm of Kostenidou et al. (2007) as a function of time for the two campaigns. This method is based on the combination of the volume distributions measured by the SMPS and the mass distributions provided from the AMS. It takes into account that the particles have a size-dependent density, but assumes that organic aerosol density is size independent. During the FAME-2008 the aerosol water

content measurements varied from 0-25% of the total mass, while during FAME-09 from 0 to 50%. The water distributions were included in the algorithm. The total density for the algorithm is given by:

$$\rho = x_{a/s}\rho_{a/s} + x_{org}\rho_{org} + x_w\rho_w \quad [4.1]$$

where $x_{a/s}$ is the mass fraction of the ammonium sulfate, x_{org} is the mass fraction of the organics, x_w is the mass fraction of the water, $\rho_{a/s}$ is the density of the ammonium sulfate or ammonium bisulfate (1.77 g cm^{-3}), ρ_{org} is the unknown organic density and ρ_w is the water density (1.0 g cm^{-3}). The algorithm matches the AMS mass distribution and the SMPS volume distribution using the organic density and CE as fitting parameters. We select the best fit, and thus the appropriate combination of organic density and CE, by minimizing the error score (Kostenidou et al., 2007). The tested range of organic aerosol density was $0.5\text{-}3 \text{ g cm}^{-3}$ and that of the CE was 0.1-2. The compared distributions were averaged approximately for 2 hours for the summer (FAME-08) and for 24 hours for the winter (FAME-09) due to the low concentrations.

During FAME-08 the average sea-salt and dust concentration measured by $\text{PM}_{1.3}$ filters was 8% of the total mass, while during FAME-09 it was 25%, excluding the days when a dust event occurred (6-8 March 2009) and the days when the wind was influenced by marine aerosols (9-13 March 2009). Figures 4.1 and 4.2 illustrate the contribution of the refractory and the non-refractory species obtained by $\text{PM}_{1.3}$ filters analysis for FAME-08 and FAME-09 campaigns. During 6-13 March 2009 there are no SMPS data because of instrumentation problems. High contribution of refractory species at the $\text{PM}_{1.3}$ filters suggests that there are alkaline compounds (e.g calcium, magnesium, sodium) at the larger sizes (above $1\mu\text{m}$) which are neutralized by sulfate. These larger particles are

not ‘seen’ by the AMS. Since most of the time the refractory species were below ~25% the sampling aerosol was mainly PM₁.

Figure 4.1: The contribution of refractory and non-refractory species for the summer campaign FAME-08. The average concentration of sea-salt and dust was 8%.

Figure 4.2: The contribution of refractory and non-refractory species for the winter campaign FAME-09. The average concentration of sea-salt and dust was 25% (excluding the days during the dust event).

4.4.2 Ambient CE and Organic Density in FAME-08

Combining the AMS and SMPS size distributions, averaging them approximately every 2 hours, the CE of the ambient aerosol was estimated at 0.85 ± 0.08 (Figure 4.3). The calculated ambient CE for this campaign is higher than the usual CE of 0.5 used in most studies (Alfarra et al., 2004; Allan et al., 2004; Drewnick et al., 2004; Zhang et al., 2005; Hogrefe et al., 2004). One explanation for this difference could be the fact that the aerosol has been usually dried before sampling in other field campaigns. When a particle dries its physical state from liquid to solid may change and this could increase the particle bounce on the vaporizer resulting in a lower CE. During FAME-08 the aerosol was highly hygroscopic since the organic fraction was highly oxidized (Chapter 5) and the inorganic mass exceeded the organic. All the above are consistent with the fact the aerosol during FAME-08 always contained water and was in a liquid state. Thus the CE is higher than in other studies.

Figure 4.3: The collection efficiency of the ambient and the thermodenuded aerosols for the full campaign of FAME-08. The average CE of the ambient and the thermodenuded aerosol was 0.85 ± 0.08 and 0.76 ± 0.09 correspondently. Our results suggest that the evaporation of the water in the thermodenuder, increases the probability of particle bounce in the AMS and therefore decreases the CE.

The average organic density of the ambient aerosol was estimated at $1.35 \pm 0.22 \text{ g cm}^{-3}$ (Figure 4.4). We did not find any trend of the organic density with the source region or a diurnal pattern. The fluctuations of the ambient organic density between 0.8 and 1.8 g cm^{-3} could be due to the different content of water. In Figure 4.5 the ambient organic density is plotted versus the water mass as measured by the AMS, the bars represent the one standard deviation. At lower water concentrations the organic density is higher. One reason for this could be that at higher water a larger fraction of these highly oxidized organic compounds may be dissolved in the water instead of being closely packed in the solid phase, thus increasing their volume and decreasing the organic aerosol density.

In order to evaluate the uncertainty of the estimated parameters by the algorithm we calculated all the solutions with error scores within 10% of the minimum error score. In Figures 4.6 and 4.7 these solutions are presented as shadows for the ambient CE and the ambient organic density respectively. Another test of the quality of the results is the comparison of the calculated AMS volume distribution with the corresponding SMPS volume distribution. An example is given in Figure 4.8.

Figure 4.4: The organic density for the ambient and the thermodenuded aerosols during month long FAME-08. The average organic density of the ambient and the thermodenuded aerosol was $1.35 \pm 0.22 \text{ g cm}^{-3}$ and $1.27 \pm 0.28 \text{ g cm}^{-3}$ respectively.

Figure 4.5: The ambient organic density as a function of the water content with one standard deviation for FAME-08. Lower water concentrations result in higher organic densities.

Figure 4.6: The ambient collection efficiency of the ambient aerosols for FAME-08. The purplish shadows represent the solutions that give error scores within 10% of the minimum error score.

Figure 4.7: The organic density of the ambient aerosols for FAME-08. The greenish shadows represent the solutions that give error scores within 10% of the minimum.

Figure 4.8: Comparison of AMS and SMPS measurements using the algorithm of Kostenidou et al. (2007). The algorithm was applied both for ambient and thermodenuded samples. The AMS and SMPS distributions were averaged approximately for 2 hours.

4.4.3 Thermodenuded CE and Organic Density in FAME-08

The analysis of the thermodenuded aerosol AMS measurements is complicated because of the partially evaporation upon heating, particle losses and the potential resistances to mass transfer during particle evaporation. The organic density and the CE of the thermodenuded aerosol that may change under these conditions are crucial for the interpretation of the thermodenuder data. Applying again the optimization algorithm of Kostenidou et al. (2007) we estimated the CE and the organic density of the thermodenuded aerosol.

The thermodenuded CE was significantly lower than that of the ambient by 10-20% during most of the study with an average value of 0.76 ± 0.09 (Figure 4.3). Our results suggest that the evaporation of the water in the thermodenuder, increases the probability of particle bounce in the AMS and therefore decreases the CE. The organic density of the thermodenuded aerosol was estimated at $1.27 \pm 0.28 \text{ g cm}^{-3}$ (Figure 4.4) and is statistically the same as that of the ambient organic aerosol ($1.35 \pm 0.22 \text{ g cm}^{-3}$).

Evaluating again the uncertainty of our approach we depict as shadows the parameter range that results to errors within 10% of the minimum error score in Figures 4.9 and 4.10. The range of the solution is wider and this may be due to the lower organic aerosol concentrations in the thermodenuder. Figure 4.8b shows an example of how well the reproduced AMS thermodenuded volume distribution matches the SMPS volume distribution.

This difference in CE should be concluded in the calculation of the remaining mass fraction of the organic aerosol in the thermodenuder, to avoid an overestimation of the organic aerosol volatility (Lee et al., 2010b).

Figure 4.9: The collection efficiency of the denuded aerosols for FAME-08. The pink shadows represent the minimum and the maximum solutions within 10% of the minimum error score.

Figure 4.10: The organic density of the denude aerosols for FAME-08. The orange shadows represent the minimum and the maximum solutions within 10% of the minimum error score.

4.4.4 Chemical Composition from the Q-AMS in FAME-08

The calculated CE of the ambient aerosol is then applied to the non-refractory PM_{10} species measured by the AMS. Figure 4.11 presents the chemical composition as measured by the AMS after the CE corrections as a function of time. Over the whole campaign the total NR- PM_{10} concentrations measured by the AMS ranged from $2 \mu\text{g m}^{-3}$ to $24 \mu\text{g m}^{-3}$; the average was $9 \mu\text{g m}^{-3}$ (Hildebrandt et al., 2010a). The periods of relatively high aerosol concentrations at this remote site are due to long-range transport of pollution to the site, for example on May 15th and 16th the pollution was originating from Megalopoli and Athens. During the campaign the aerosol originated from different sources: Europe, Africa, Greece and marine as well (Pikridas et al., 2010). The largest fraction of the sampled aerosol was ammonium sulfate and ammonium bisulfate, then organics, water, and very low nitrate.

Figure 4.11: The time series (9 minutes average) of ambient sulfate, ammonium, organics and nitrate measured by the AMS after applying the estimated CE from the AMS-SMPS algorithm (FAME-08). The total concentration ranged from $2 \mu\text{g m}^{-3}$ to $24 \mu\text{g m}^{-3}$, while the average was $9 \mu\text{g m}^{-3}$ (Hildebrandt et al., 2010a).

In Figure 4.12, and 4.13 we compare the corrected AMS sulfate and ammonium data to the 24-hours $PM_{1.3}$ filter measurements ($R^2 = 0.95$ and 0.84 respectively). AMS sulfate measurements also agree well with the steam sampler data (Figure 4.14). The correlation was good resulting in an $R^2 = 0.79$ (not shown). The agreement among all three instruments is within the corresponding uncertainties of the measurements.

Figure 4.12: Sulfate mass comparison between $PM_{1.3}$ filters and the AMS mass concentrations. Also shown the 1:1 line. The agreement is quite good ($R^2=0.95$).

Figure 4.13: Ammonium concentration comparison between PM_{1.3} filters and the AMS mass concentrations ($R^2=0.84$).

Figure 4.14: Time series of sulfate mass concentration measured by the steam sampler and the AMS during FAME-08. The agreement is satisfactory ($R^2=0.79$).

Figure 4.15 shows the average chemical AMS mass distributions for the ambient aerosol for the whole FAME-08 campaign. The modes of the different aerosol species (sulfate, organics, ammonium, water and nitrate) are all at similar diameters, implying that the PM_{10} particles during FAME-08 had all similar composition. This is consistent with remote sources of this aerosol, and with atmospheric processing and mixing before sampling at Finokalia (Hildebrandt et al., 2010a).

Figure 4.15: The FAME-08 campaign-average ambient time-of-flight size distributions of the dry aerosol species measured by the AMS, versus vacuum aerodynamic diameter.

4.4.5 CE and Organic Density in FAME-09

During FAME-09 (winter) the average NR-PM₁ aerosol concentrations as measured by the AMS was 2.9 $\mu\text{g m}^{-3}$ (Hildebrandt et al., 2010a and b). Thus the compared AMS and SMPS distributions were averaged for 24 h. Using again the approach of Kostenidou et al. (2007) the calculated CE of the ambient aerosol was 0.64 ± 0.13 (Figure 4.16). This is lower than in the summer campaign and implies that the particles had different properties. Instrumental differences (a different Q-AMS was used in these two campaigns) may also explain the discrepancy. One reason for the different particle properties inside the AMS could be their chemical composition. The ratio of OA:SO₄²⁻ was close to unity for FAME-09, while for FAME-08 it was around 0.5. Thus the fraction of the more hygroscopic species such as sulfate was lower in the winter. During the winter the lower concentrations of the OH radical resulted in more variable and lower extent of oxidation of the organic aerosol, and thus in less hygroscopic organic compounds. The frequent precipitation contributed to the removal of the existing aged OA and the transportation of new less oxidized OA.

The average thermodenuded CE was estimated at 0.58 ± 0.14 (Figure 4.16). The thermodenuded CE was in general a little lower or equal the ambient, except for the beginning of the campaign.

The average organic density of the ambient organic aerosol was estimated at $1.14 \pm 0.36 \text{ g cm}^{-3}$ (Figure 4.17). The average density of the denuded OA was $1.06 \pm 0.34 \text{ g cm}^{-3}$ (Figure 4.17).

Figure 4.16: The collection efficiency of the ambient and thermodenuded aerosol for the campaign of FAME-09. The average CE of the ambient and thermodenuded aerosol was 0.64 ± 0.13 and 0.58 ± 0.14 respectively.

Figure 4.17: The organic density of the ambient and thermodenuded aerosol for the full campaign of FAME-09. The average organic density of the ambient and thermodenuded aerosol was $1.14 \pm 0.36 \text{ g cm}^{-3}$ and $1.06 \pm 0.34 \text{ g cm}^{-3}$ respectively.

Figures 4.18 and 4.19 show the values of CE and organic density that result in solutions within 10% of the minimum error score for the ambient CE and the ambient organic density respectively, while Figures 4.20 and 4.21 the uncertainties of the thermodenuded CE and the thermodenuded organic density.

Figure 4.18: The collection efficiency of the ambient aerosols for FAME-09. The purplish shadows represent solutions within 10% of the minimum error score.

Figure 4.19: The organic density of the ambient aerosols for FAME-09. Again the greenish shadows are solutions within 10% of the minimum error score.

Figure 4.20: The collection efficiency of the denuded aerosols for FAME-09. The pink shadows show solutions within 10% of the minimum error score.

Figure 4.21: The organic density of the thermodenuded aerosols for FAME-09. The orange shadows represent solutions within 10% of the minimum error score.

4.4.6 Chemical Composition from the Q-AMS in FAME-09

In the next step we apply the estimated ambient CE to the mass concentrations measured by the AMS. Figure 4.22 illustrates the chemical composition of the dry NR-PM₁ species measured by the AMS. The fraction of the organics is almost the same with the sulfate. There is much less ammonium and practically no nitrate. The average total dry NR-PM₁ during FAME-09 was $2.8 \mu\text{g m}^{-3}$ ranging between 0.1 and $7.6 \mu\text{g m}^{-3}$. These concentrations are approximately three times lower than the values measured during FAME-08. This can be explained by the much more frequent precipitation during FAME-09, the lower temperatures and the lower photochemical activity during the winter. The aerosol was more variable than in FAME-08 and this is probably due the variable photochemistry (there were sunny days but also days when it snowed in Crete) and thus the oxidation conditions.

Figure 4.22: Time series (1 hour averages) of ambient NR-PM₁ sulfate, ammonium, organics and nitrate as seen by the AMS, after applying the estimated CE from the AMS-SMPS algorithm. The average dry PM₁ concentration was $3 \mu\text{g m}^{-3}$, about 3 times lower than during FAME-08.

In Figure 4.23 we compare the sulfate from 24-hours $PM_{1.3}$ filters to the AMS sulfate after applying the correction of the ambient CE. The correlation coefficient is $R^2=0.78$. The AMS, after the CE application, underestimates the sulfate concentrations compared to the filters. The explanation for this maybe lies in the fact that the average contribution of the refractory compounds during FAME-09 was approximately 25%, so a part of the aerosol at sizes higher than $1\ \mu m$ is salt (sodium, magnesium and/or calcium) neutralized by sulfate. Thus the $PM_{1.3}$ filters ‘see’ more sulfates than the AMS which measures PM_1 particles.

Figure 4.23: Sulfate mass comparison between $PM_{1.3}$ filters and the AMS mass concentrations for FAME-09. The agreement is good ($R^2=0.78$, slope = 1.08). The underestimation of the AMS could be due to the refractory species (above $1\ \mu m$) such as calcium, magnesium and sodium that are neutralized by sulfate. This sulfate is measured by the $PM_{1.3}$ filters but not by the AMS.

4.5 Conclusions

The SMPS-AMS size distribution matching algorithm of Kostenidou et al. (2007) can be applied not only to laboratory but also to ambient AMS and SMPS data, estimating the organic density and the CE of the AMS. For FAME-08 the calculated average ambient AMS CE was 0.85 ± 0.08 , while the thermodenuded CE was 0.76 ± 0.09 . The lower CE in the thermodenuder is probably due to the water losses that can increase the particles bounces on the vaporizer and therefore decreases the CE. For FAME-09 the estimated ambient AMS CE was 0.64 ± 0.13 while the thermodenuded one 0.58 ± 0.14 . This is consistent with the lower contribution of the hygroscopic inorganic species and the photochemistry of this season that lead to less aged and thus less hygroscopic organic compounds. The intercomparisons between AMS and other systems showed quite good correlation for FAME-08 and a reasonable correlation for FAME-09. The ambient organic density was computed at $1.35 \pm 0.22 \text{ g cm}^{-3}$, while the thermodenuded at $1.27 \pm 0.28 \text{ g cm}^{-3}$. The fluctuations of the ambient organic density are likely related with the water content of the aerosol. For FAME-09 the ambient organic density was estimated at $1.14 \pm 0.36 \text{ g cm}^{-3}$, while the thermodenuded at $1.06 \pm 0.34 \text{ g cm}^{-3}$.

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Chapter 5

Measurements of the Organic Aerosol Chemical Composition during the Finokalia Aerosol Measurement Experiment-2008: Volatility Measurements

This work is part of the following publication:

Lee, B.-H., Kostenidou, E., Hildebrandt, L., Riipinen, I., Engelhart, G. J., Mihalopoulos, N., Prevot, A., S. H., Baltensperger, U., and Pandis, S. N. (2010) Measurement of the Ambient Organic Aerosol Volatility Distribution: Application during the Finokalia Aerosol Measurement Experiment (FAME-2008), *Atmospheric Chemistry and Physics* (in preparation).

5.1 Introduction

Atmospheric aerosol consists of a variety of both inorganic and organic compounds. Organic aerosol (OA) may contribute to global submicron particle mass 20-90% (Zhang et al., 2007). Their short lifetimes and wide range of particle sizes, chemical compositions and physical properties however make their study very complex (McMurry, 2000). One important property is their volatility, which is defined by the chemical properties of the condensed compounds. The photochemistry can lower the vapour pressures of the organic gaseous species and move them or part of them into the particulate phase (Went, 1960) and thus contribute significantly to the global aerosol composition and concentration (Kanakidou et al., 2005). Then, OA can re-evaporate and get further oxidized in the gas phase or it can react heterogeneously in the particle phase (chemical aging). Thus, volatility encompasses useful information about the chemical history of the particle (Jonsson et al., 2007).

One common technique for volatility measurements is the use of a thermodenuder (Dinger et al., 1970; Hoppel et al., 1973). A thermodenuder usually consists of two parts, one heating and one cooling, which are usually tubes from stainless steel. As the particles are heated, the more volatile species evaporate, leaving behind the less volatile compounds in the particulate phase. The sample after the thermodenuder can then be measured and analyzed by various instruments. Over the years a number of different thermodenuder designs have been proposed. For example Butcher et al. (2001) added in the cooling section activated charcoal as a gas denuder to avoid re-condensation. An et al., (2007) used a tube placed in an oven as the heating part to reach high temperatures at high residence times. The characteristics of these thermodenuders can be quite different. For example, the residence time of the sample in the heating section can vary from 0.6 s (Jonsson et al., 2007) to 60 s (Lee et

al., 2010a). However, An et al. (2007) suggest that because of the potential resistances to mass transfer from the particulate to the gas phase, the thermodenuders need to be operated at a range of residence times.

In the last years many groups employed an Aerosol Mass Spectrometer (AMS) after a thermodenuder. With this set up one can relate the aerosol composition to their volatility (Grieshop et al., 2009; Huffman et al., 2009) or to separate the mass spectrum as a function of the volatility (Kostenidou et al., 2009). In this work we combine a variable residence time thermodenuder with a Q-AMS and an SMPS in order to study the volatility of the OA during summer 2008 (FAME-08). We estimate the organic volatility introducing a new method to correct for the various challenges of ambient-thermodenuded AMS measurements.

5.2 Experimental

5.2.1 Thermodenuder and AMS at the Finokalia Site

A thermodenuder was used with a Q-AMS and an SMPS for volatility measurements during FAME-08. The thermodenuder used is based on the design of Wehner et al. (2002) and An et al. (2007). It consists of two sections which are two stainless steel tubes; a heating zone followed by a cooling section and organic vapour adsorption. The heating part is wrapped with a heating tape which controls the temperature in the heating tube. For the vapour adsorption activate carbon is used. The thermodenuder set up is described in more detail in Lee et al. (2010b). The temperature ranged between 25 and 140°C. The centreline residence times during FAME-08 were 14 and 105 s.

5.3 Thermodenuder-AMS Data Analysis

As the aerosol passes through the thermodenuder three things may happen: partially evaporation upon heating, particle losses in the thermodenuder and potential resistances to mass transfer during particle evaporation. All of the above may also change the average CE of the AMS and the average organic density. Thus the analysis of ambient and thermodenuded AMS measurements is complicated. Here we introduce an approach that addresses these problems.

5.3.1 Collection Efficiency and Organic Density during FAME-08

The CE of the AMS is a function of the aerosol shape, size, morphology and chemical composition (Canagaratna et al., 2006). After the particles exit the thermodenuder the CE may also change due to loss of water, changes in particle shape or different behavior on the AMS vaporizer of the less volatile species or a combination of these. The organic density may also change after the aerosol has passed through the thermodenuder.

Using the algorithm of Kostenidou et al. (2007) and including the water distributions, we calculated the CE and the organic density both for the ambient and the thermodenuded samples. The whole procedure is described in Chapter 4 section 4.4.1. The AMS CE decreased approximately 10% for the aerosol that passed through the TD but the organic density for the thermodenuded aerosol was similar to that of the ambient particles.

5.3.2 Particle Losses inside the Thermodenuder for FAME-08

Inside the thermodenuder particle losses are caused by the contribution of three factors: sedimentation, diffusion and thermophoresis. Sedimentation takes place as the particle size increases and diffusion as the particle size decreases. Thermophoresis

depends mostly on temperature (Burtcher et al., 2001). The particles during FAME-08 were most of the time larger than 50 nm (Pikridas et al., 2010) and the size distribution was quite stable as the aerosol was aged (Hildebrandt et al., 2010). This stability resulted in constant number losses in the TD, approximately 15% of the total (Lee et al., 2010b). The losses were not strongly size-dependent but more strongly temperature-dependent. This assumption will be evaluated using the calculated CE and organic density.

5.3.3 Algorithm Consistency Check for FAME-08

The consistency check can be made by calculating the thermodenuded SMPS number and volume distributions using the ambient corresponding distributions and then comparing them with the actual SMPS measurements after the thermodenuder. This approach also requires the measured by the AMS NR-PM₁ concentrations, the estimated number losses, the OA density, and the CE of the AMS.

The aerosol volume fraction remaining (VFR) after the thermodenuder, including the corrections for thermodenuder losses, the varying CE and density, can be extracted using the AMS measurements as:

$$VFR = \left[\frac{[OA]_{TD} / \rho_{org_TD} + [Sulfates]_{TD} / \rho_{a/s} + [Water]_{TD} / \rho_w}{[OA]_{amb} / \rho_{org_amb} + [Sulfates]_{amb} / \rho_{a/s} + [Water]_{amb} / \rho_w} \right] \cdot \frac{CE_{amb}}{CE_{TD}} \cdot \frac{1}{1 - f_N} \quad [5.1]$$

where subscript *TD* denotes a thermodenuded sample, subscript *amb* represents an ambient sample, *[OA]* is the mass concentration of organic aerosol, *[Sulfates]* is the mass concentration of ammonium sulfate or bisulfate, *[Water]* is the mass concentrations of water, ρ_{org} is the density of organic aerosol that is estimated by the

optimization algorithm of Kostenidou et al. (2007), $\rho_{a/s}$ is the density of the ammonium sulfate, ρ_w is the water density, CE_{amb} is the CE of AMS for the ambient sample, CE_{TD} is the CE for the thermodenuded sample, and f_N is the fraction of particle number losses in the TD, estimated based on the ambient and heated SMPS number distributions.

The diameter of an evaporated particle, $D_{p,TD}$ is given by:

$$D_{p,TD} = D_{p,amb} (VFR)^{1/3} \quad [5.2]$$

where $D_{p,amb}$ is the diameter of the ambient aerosol. Then we can calculate the thermodenuded number distribution, $n_n(D_{p,TD})$:

$$n_n(D_{p,TD}) = n_n(D_{p,amb}) \cdot \left(\frac{dD_{p,amb}}{dD_{p,TD}} \right) \cdot (1 - f_N) \quad [5.3]$$

where $n_n(D_{p,amb})$ is the ambient number distribution as measured by the SMPS.

The thermodenuded volume distribution, $n_v(D_{p,TD})$, can be written as:

$$n_v(D_{p,TD}) = n_v(D_{p,amb}) \cdot \left(\frac{dD_{p,amb}}{dD_{p,TD}} \right) \cdot (1 - f_N) \quad [5.4]$$

where $n_v(D_{p,amb})$ is the ambient volume distribution as seen by the SMPS.

Next we compared the estimated evaporated number and volume distributions resulting from equations [5.3] and [5.4] to the actual thermodenuded number and volume distributions, respectively. Figures 5.1 and 5.2 illustrate some typical results.

Figure 5.1: Number and volume distributions of ambient aerosol and thermodenuded aerosol while TD was operated at 106°C during 1-2 am at June 2nd. Also plotted is the predicted aerosol distribution accounting for both the changes in the AMS CE and density and the losses in the TD system. The fraction of number losses (f_N) was 0.140, and the collection efficiencies for the TD and ambient samples were 0.85 and 0.90, respectively (Lee et al., 2010b).

Figure 5.2: Number and volume distributions of ambient aerosol and thermodenuded aerosol while TD was operated at 108°C during 5-6 pm at June 3rd. Also plotted is the predicted aerosol distribution accounting for both the changes in the AMS CE and density and the losses in the TD system. The fraction of number losses (f_N) was 0.153, and the collection efficiencies for the TD and ambient samples were 0.80 and 0.95, respectively (Lee et al., 2010b).

The predicted thermodenuded distributions are in agreement with the measured evaporated distributions for all particle diameters. This implies that (1) the losses were likely size independent during FAME-08, (2) the approach for the post-correction for the losses inside the thermodenuder and the changes in the AMS CE and organic aerosol density during heating is valid, (3) the measurements from the AMS and SMPS are consistent with each other and organic information from the AMS can be used to estimate the actual evaporated fraction of organic aerosol as a function time and temperature for the FAME-2008 period.

5.4 Results and Discussion

5.4.1 Volatility of Organic Aerosols during FAME-08

For the post-correction of the data 24-min averaged values of CE and organic density are used. In Figure 5.3 the organic mass fraction remaining (MFR) is plotted versus the temperature in the thermodenuder and the effect of these corrections on the volatility of organic aerosol is clear: the changes in the AMS CE and organic density during heating and the losses inside the thermodenuder results in ~20% underestimation of the evaporated mass fraction. At higher temperatures the differences between the corrected and uncorrected data are greater (~30% differences in MFR) since at higher temperature the particle losses inside the TD are greater.

The organic aerosol during FAME-2008 was much less volatile than the laboratory-generated α -pinene SOA (e.g. Lee et al., 2010b) of the same average size (Figure 5.3). The explanation for this is the fact that during FAME-08 the organic aerosol was highly oxidized as the organic mass spectrum suggest (Hildebrandt et al., 2010). In Figure 5.4 we present a mass spectrum from fresh α -pinene SOA and the average mass spectra for FAME-08. The main difference is that during FAME-08 the

contribution of m/z 44, associated to oxidized organic aerosol, to the organic spectrum during FAME-08. Using a multi-component organic aerosol evaporation model and the volatility-basis set Lee et al. (2010b) showed that the organic aerosol during FAME-2008 is more than one order of magnitude less volatile than laboratory-generated α -pinene SOA.

Figure 5.3: Mass fraction remaining after heating in the TD (for 14 s) as a function of temperature for uncorrected TD-AMS data (blue), corrected for the losses in TD and the changes in AMS collection efficiency and density data (red) during FAME-2008. Each data point is the average of 30 MFR data sets, which is 24 min averaged. We also plotted the thermogram of fresh lab-generated α -pinene SOA (green) with mass concentration of approximately $10 \mu\text{g m}^{-3}$ and size of approximately 250 nm (Lee et al., 2010b).

Figure 5.4: (a) The mass spectrum of fresh α -pinene SOA aerosol and (b) the average mass spectrum for FAME-08. The much higher signal fraction of m/z 44 during the summer campaign denotes that the aerosol was highly oxidized.

5.5 Conclusions

The volatility of OA during FAME-08 was estimated. We used the ambient and the thermodenuded organic density and the CE of the AMS, as calculated in Chapter 4, for post-corrections in order to avoid the overestimation of the OA volatility. We evaluated this approach and we found it valid, thus the organic information from the AMS can be used to calculate the real evaporated organic fraction as a function of time and temperature for the FAME-08 data. The OA during the summer is quite

uniform and highly oxidized due to the photochemistry. Further, the organic aerosol during FAME-2008 is more than one order of magnitude less volatile than laboratory-generated α -pinene SOA (Lee et al., 2010b).

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Chapter 6

**Steam Sampler Measurements of both
Particulate and Gaseous Concentrations of
Semivolatile Inorganic Aerosol Components**

6.1 Introduction

Atmospheric aerosol plays an important role in chemical and physical processes in the atmosphere such as cloud formation, visibility, heterogeneous chemistry and climate forcing (Hizenberger et al., 1999, Jacob et al., 2000). They can also have an adverse effect on human health (US Environmental Protection Agency, 1996, Pope et al., 2002). The particle chemical composition is required in order to understand the sources, atmospheric transformation and the fate of ambient aerosols. The traditional measurement method is based on the collection of particles on filters and off-line extraction and analysis.

Although traditional filter methods are used widely, they have many disadvantages. The sampling times vary from several hours to days and they both labor intensive and expensive. Preparation of filters, setting-up of the samplers, collection of the samples, extraction and analysis take considerable time and limit the frequency of measurements. Further, off-line techniques may lead to artifacts particularly for semivolatile aerosol species, because of interaction between the gas-phase and the filter material (or the particles on the filter). Vapors can be adsorbed on the filter or on the particles already collected on the filter (positive artifact) and particulate material already on the filter may evaporate.

Except for the filter-based methods, several semi-continuous approaches have been developed and used in recent years. Ambient particulate sulfate and nitrate monitors, based on the humidified particle impaction with subsequent flash volatilization (Wittig et al., 2004) can provide 10-minute resolution measurements. Flame photometry has been used as well for sulfate quantification (Allen et al., 1984, Lippmann et al., 2000). Kolb et al. (2000) used an approach involving an aerodynamic particle time-of-flight to select the particle size range, followed by

thermal vaporization and analysis using a mass spectrometer. The disadvantage of these approaches is that they usually target only one aerosol component at a time. One needs therefore several instruments to still get a partial view of the aerosol composition.

Recently several instruments referred as ‘steam collector devices’ have been developed. This method is based on aerosol particle growing into droplets in a supersaturated environment of water vapor. The grown particles are collected by inertial techniques and the sample is analyzed on- or off-line. The Steam-Jet Aerosol Collector (SJAC) (Khlystov et al., 1995, Slanina et al., 2001) collects grown particles in two glass cyclones and the liquid sample is then analyzed in two ion chromatographers (IC’s). Kidwell and Ondov (2001) developed a technique with high aerosol sample flow rate (170 l min^{-3}) which concentrates and then collects the droplets combining a virtual with a real impactor. This system measures traces of metals in aerosols using Graphite Furnace Atomic Absorption Spectroscopy. Another variation of the same idea developed by Weber et al. (2001) is the particle-into liquid sampler (PILS) where the particles grow in a growth chamber and then are collected with an impactor. PILS is coupled with two IC’s and provides on-line measurements of inorganic aerosol species. This instrument is now commercially available.

Simon and Dasgupta (1995a, 1995b) developed a system for detection of particulate and gas phase HONO and HNO₃. The aerosol is mixed with steam and then grows in a cooled stainless steel maze, while the gases are collected in a system with a wetted wall parallel plate diffusion denuder. The liquid samples of particulate and gas phase were then alternatively measured by an IC system.

In this work we continue the development of the steam-jet aerosol collector to measure semi-continuously all inorganic aerosol components and the gas-phase

concentrations of their semivolatile components (NH_3 , HCl , HNO_3 , HCl , etc.). This approach is based on the SJAC (Khlystov et al., 1995) system sampling alternatively from a denuded and an undennuded line. The advantage of our technique is that it measures the concentrations in both phases with a minor increase in system complexity.

6.2 Steam Sampler Description

The general steam sampler system is shown in Figure 6.1. It consists of 3 main parts: (1) a sampling system alternating between an undenuded and a denuded line, (2) a steam-jet aerosol collector and (3) a set of two ion chromatographs (ICs).

Figure 6.1: Schematic of the general steam sampler system.

6.2.1 Alternation between Denuded/Undenuded Sampling Lines

The system is equipped with 2 lines: one with a set of two annular denuders and one without. Two valves moving by a servo motor control automatically the sample air flow direction alternating every period Δt . A period of 30 min has been used in the initial tests of the system. Through undenuded line both particulate and gas phase pollutants enter the system allowing the measurement of the corresponding total concentrations. The denuded line removes the gaseous species allowing the measurement only of the particulate phase. The gas phase concentration can then be calculated from the subtraction of the denuded (particulate) from the undenuded (particulate+gases) concentration.

A set of annular glass diffusion denuders (URG-2000) is used for the removal of the water soluble gaseous species. One denuder is coated with a 1% sodium carbonate and 1% glycerol solution for removal of acids gases (SO_2 , HNO_3 , HONO and HCl) and the second with a solution of 2% citric acid and 1% glycerol for removing basic gases (NH_3). The denuders are close to the steam jet aerosol collector inlet so the denuded aerosol does not have time to evaporate because of the gases removal.

We tried to minimize as possible the metal tubing and replace it with Teflon to avoid HNO_3 losses, because HNO_3 is rapidly deposited on metal surfaces. We used a Teflon-coated $\text{PM}_{2.5}$ cyclone (URG) at 16.7 L min^{-3} as well.

6.2.2 The Steam-Jet Aerosol Collector

The SJAC consists of a steam generator, growth chamber and two cyclones (Khlystov et al., 1995) as shown in Figure 6.2. The air stream from ambient enters the growth chamber made of glass and is mixed with the steam coming from the steam generator. The steam generator is a three-necked glass flask placed into an electrical

nest. Through one of the necks distilled water is constantly pumped by a peristaltic pump with a rate of 0.8 ml min^{-1} . As the water boils the steam is transferred to the mixing reservoir through PTFE tubing.

Figure 6.2: Schematic of the steam-jet aerosol collector.

Into the mixing chamber (40 cm^3) the water supersaturation makes the particles grow into droplets of $1\text{-}7 \text{ }\mu\text{m}$ diameter which are then collected by two glass cyclones in series. A peristaltic pump constantly pumps out the liquid sample collected from the two cyclones into a testing tube. A known concentration solution of LiF with a known flow rate (usually $0.1\text{-}0.3 \text{ ml min}^{-3}$) is introduced into the tube as an internal standard. The volume of the liquid sample in this tube is $2\text{-}3 \text{ ml}$ and is constantly pumped out by a second peristaltic pump by two lines at a rate of $0.222 \text{ ml min}^{-1}$ each in order to be analyzed by the two IC's. The tubing used for the above lines is made of PTFE and marprene.

6.2.3 The Ion Chromatography Systems

The concentration of the major inorganic ionic compounds of the collected samples is analyzed using two computer-controlled ion chromatography systems (Metrohm 761 Compact IC). The anions and cations IC's are equipped with a 200 and 500 μL loop, a separation column (Metrosep A supp 5 for anions, Metrosep C2 100 for cations), a suppressor (only for anions), and a conductivity meter. The analysis is performed with isocratic elution using an eluent of 3.2 mM Na_2CO_3 and 1mM NaHCO_3 for the anions and an eluent of 4.0 mM tartaric acid and 0.75 mM dipicolinic acid for the cations. The flow rates of the eluents are 0.7 ml L^{-1} (anions) and 1.0 ml L^{-1} (cations). The resolution of the above system is 20 min.

For the calculation of the ambient aerosol concentration from IC liquid concentration measurement we use the following equation:

$$[C_g] = \frac{[C_L]Q_L[C_{Li1}]}{[C_{Li2}]Q_a} \quad [6.1]$$

where $[C_g]$ is the ambient concentration in $\mu\text{g m}^{-3}$, $[C_L]$ is the concentration of the liquid sample in $\mu\text{g L}^{-1}$, $[Q_L]$ is the flow rate of the LiF solution, $[C_{Li1}]$ is the Li concentration of the LiF solution, $[C_{Li2}]$ is the Li concentration in the measured cation chromatograph and $[Q_a]$ is the volumetric flow rate of sample air to the instrument. The limits of detection based on the smallest peak we could reliably integrate was similar to the calculated limits of detection, ranging from 0.05 $\mu\text{g m}^{-3}$ for anions (sulfate, nitrite, nitrate and chloride) to 0.5 $\mu\text{g m}^{-3}$ for cations (ammonium, sodium, potassium, calcium and magnesium)

6.3 Results and Discussion

We tested this system in our laboratory in the Chemical Institute in Patra sampling ambient $\text{PM}_{2.5}$ aerosol. The surrounding area is agricultural ~ 10 km away from the center of Patras and approximately 3 km from the coast. During the measurement period February and March of 2010 the inorganic $\text{PM}_{2.5}$ concentrations were below $12 \mu\text{g m}^{-3}$. The measured by the steam sampler components in this location included ammonium, nitrate, sulfate, nitrite, sodium, calcium, chloride, etc.. The concentrations of calcium, sodium, potassium and phosphate were very low. Aerosol samples were also collected on Teflon filters (every 3 to 7 h) at the same time for comparison with the steam-sampler aerosol measurements. Here we discuss the results of three experiments performed on 28 February (12:00-19:00), 01 March (16:00-22:00) and 02 March (10:00-18:00) 2010.

6.3.1 Ammonium and Ammonia

Ammonium measurements for the three measurement periods are shown in Figure 6.3. The denuded and the undenuded concentrations of ammonium are in $\mu\text{g m}^{-3}$. The concentrations in all the undenuded samples are higher than the denuded. Subtracting the denuded (particles) from the undenuded (gas+particles) values we can estimate the gaseous NH_3 . Figure 6.4 shows the NH_3 concentrations (in ppb) for the three experiments, where the NH_3 varies from 4 to 80 ppb. This is consistent with the fact that the region around the FORTH Institute is agricultural, with several ammonia sources: animal waste, emissions from soil due to ammonification of humus and evaporation of NH_3 -based fertilizers.

Evaluating how well the system measures the NH_3 we compared the results of the thermodynamic model ISORROPIA (Nenes et al., 1998) to the measurements. This

model uses as inputs the temperature and the RH, the total (gas and particle phase) of ammonium, nitrate and chloride and the particulate phase concentration of sulfates and sodium. This model calculates the partitioning between gas and particle phase for the nitrate, ammonium and chloride so it tests the consistency of our measurements with thermodynamic theory. For ammonia the predicted results of this algorithm are illustrated in Figure 6.4 with brown dash lines. The measured and the predicted concentrations are in a good agreement ($R^2 = 0.995$, slope = 0.994).

6.3.2 Nitrate and Nitric Acid

The concentrations of the denuded and the undenuded samples were much lower than the ammonium values and very similar to each other during all three measurement periods. In Figure 6.5 we present the total nitrate and the particulate nitrate for the experiments on 28 February, 1 and 2 March 2010. In some cases the denuded sample was higher than the undenuded. This suggests that the HNO_3 was at very low concentrations during that period because all of it had been transferred to the particulate phase. Nitric acid is the major oxidation product of NO_x in the atmosphere. NO_x is mainly emitted by vehicles through fuel combustion. The FORTH Institute area is a suburban with no traffic, so the NO_x levels are expected to be low. Thus, the results are consistent with the characteristics of the sampling location.

In Figure 6.6 the estimated HNO_3 concentration (in ppb) for the three experiments is shown. In many cases the HNO_3 estimations are below zero reflecting the uncertainty of our approach (estimated at 0.5 ppb). ISORROPIA predictions for HNO_3 (Figure 6.6) are however above zero (0.2-0.8 ppb). Comparing the measured with the predicted concentrations we observe that in the first and the third experiment

the measured and the predicted values follow the same trend. This implies that our system is close to the detection limit for HNO_3 , which is around 0.5 ppb.

Figure 6.3: Undenuded (gas NH_3 + particle NH_4^+) and denuded (particle NH_4^+) ammonium concentration as measured by the steam sampler. The black dashed line is the particulate ammonium concentration measured by the traditional filter-based method.

Figure 6.4: Gas NH_3 (squares) calculated as the difference between denuded and undenuded concentrations. These results are in a good agreement with the predicted NH_3 from the thermodynamic model ISORROPIA (dashed line).

Figure 6.5: Undenuded (gas HNO_3 + particle NO_3^-) and denuded (particle NO_3^-) nitrate concentration as measured by the steam sampler. The filter measurements (black dashed line) agree well with the particulate phase of the steam sampler.

Figure 6.6: Gas HNO_3 (squares) arrives from the difference between denuded and undenuded concentrations. These results are in a good agreement with the predicted NH_3 from the thermodynamic model ISORROPIA (dashed line).

6.3.3 Nitrite and Nitrous Acid

Except for NH_3 and HNO_3 we can also measure with this approach the HONO concentrations in the atmosphere. Figure 6.7 shows the denuded and the undenuded concentrations for the nitrite. Although the measured concentrations are very low (below $1 \mu\text{g m}^{-3}$) the total nitrite is always higher than the particulate nitrite. This suggests that the nitrite aerosol concentration was much lower than the gas HONO concentrations something consistent with aerosol thermodynamics Figure 6.8 presents the HONO concentration in ppb.

6.3.4 Sulfate

The denuded particulate sulfate measurements by the steam sampler agree well with filter measurements. However, the undenuded values are significantly higher. This suggests that sulfate is formed in our system when no denuders are present to remove the gas-phase SO_2 . This has been observed in other studies and has been explained by the rapid oxidation of dissolved sulfur dioxide to sulfate in water by hydrogen peroxide and ozone (at high pH). This is not a problem for our system; one should use just the denuded line sulfate measurements.

Figure 6.7: Undenuded (gas HONO + particle NO_2^-) and denuded (particle NO_2^-) nitrite concentration by the steam sampler. The black dashed line is the filter measurements and agrees with the particulate phase of the steam sampler.

Figure 6.8: Gas HONO from the difference between denuded and undenuded concentrations. Although at low concentrations, HONO is clearly detectable by the steam sampler.

Figure 6.9: Undenuded and denuded sulfate concentration as seen by the steam sampler. The difference between the denuded and the undenuded measurements arise from sulfate formation in the system from gas-phase SO_2 , and thus only denuded samples have to be taken account.

6.4 Conclusions

In this work we present a new steam sampler-based technique for atmospheric particulate and gaseous measurements. Testing the approach at ambient conditions we were able to measure together with the inorganic aerosol composition the gas-phase concentrations of NH_3 , HONO and very low HNO_3 . The particulate phase concentrations agreed well with traditional filter-based measurements and the gas-phase concentrations were consistent with the predictions of the thermodynamic model ISORROPIA. While concentrations of gas-phase HONO as low as 0.1 ppb were detected the detection limit for HNO_3 appears to be close to 0.5 ppb. This smaller sensitivity to nitric acid is probably due to interferences due to its adsorption on surfaces of the sampler. During the measurements practically all the nitric acid was in the particulate phase due to its reaction with ammonia and the formation of ammonium nitrate. More tests should be done in a polluted urban area during the summer where the NO_x and thus the HNO_3 levels are higher.

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Chapter 7

Summary and General Conclusions

The overall goal of this thesis was the improvement of our understanding of the physical and chemical properties of the atmospheric aerosols. In Chapter 2 a method that combines an AMS, an SMPS and a thermodenuder to characterize the SOA mass spectrum as a function of the volatility was presented. This approach was applied on α -pinene, β -pinene and limonene SOA. For the less volatile SOA the signal fraction of m/z 44, and thus the concentration of CO_2^+ , is significantly higher. This suggests that the less volatile compounds are more oxidized. At high NO_x conditions the produced SOA is less oxidized than at low NO_x conditions, while increasing the relative humidity levels the products are more oxidized for limonene SOA but for α - and β -pinene SOA has little effect. Based on the volatility basis-set the SOA mass spectrum was then deconvoluted in low, medium and high volatility species mass spectra. The spectrum of the surrogate component with the lower volatility from α - and β -pinene SOA is quite similar to that of ambient oxygenated organic aerosol. This implies that part of the AMS mass spectra discrepancies between the laboratory and the field is due to differences of SOA composition with volatility.

In Chapter 3 an algorithm for the calculation of the organic aerosol density was introduced combining an AMS and an SMPS. This method takes account changes in particle composition with size. This method was applied on SOA formed by α -pinene, β -pinene and d-limonene ozonolysis and the estimated organic density was in the range of 1.4-1.65 g cm⁻³. The high density that was estimated suggests that the SOA is likely in a solid or waxy phase. A density of 1.4 – 1.65 g cm⁻³ for organics is consistent with ambient measurements of the overall particle density. This density is significantly higher than the densities of the few known α -pinene photo-oxidation products (e.g., the density of pinic acid is 1.09 g cm⁻³). Based on our results, SOA yields in smog chamber experiments may be a lot higher (up to 50%) than the

currently assumed values. The above algorithm can also estimate the CE of the AMS continuously. Assuming spherical particles this method can also be applied to primary organics and to ambient particles as well.

Since in aerosol science both laboratory studies and field measurements are equally important two field campaigns took place at the EUSAAR station of Finokalia in the summer of 2008 (FAME-08) and in winter the of 2009 (FAME-09) (Chapter 4). The instrumentation employed during these campaigns included among others an AMS an SMPS and a thermodenuder. Applying the algorithm that matches the AMS and the SMPS data, the ambient and the thermodenuded organic density and the CE of the AMS were determined. For FAME-08 the average organic density for the ambient aerosol was estimated at $1.35 \pm 0.22 \text{ g cm}^{-3}$. The fluctuations between 0.8 and 1.6 g cm^{-3} are likely connected to the water content: at higher water concentrations the organic density is lower probably because the highly oxidized organic compounds observed in Finokalia may be dissolved in the water instead of being closely packed in the solid phase, thus increasing their volume and decreasing the organic aerosol density. The thermodenuded density of the OA was estimated at $1.27 \pm 0.28 \text{ g cm}^{-3}$ and is statistically the same as that of the ambient organic aerosol. The average ambient CE was estimated at 0.85 ± 0.08 . The higher than the usual value can be explained by the fact the particles were always liquid and the organic aerosol was highly oxidized and thus hygroscopic. The average thermodenuded CE was 10-20% lower (0.76 ± 0.09) because of the water evaporation in the thermodenuder which increases the particles bounces in the AMS. Applying the ambient CE to the AMS data the correlation between the AMS and other instrumentation was quite good. During FAME-09 the average ambient CE was 0.64 ± 0.13 lower than the summer CE. This suggests that the particles had different properties. One reason could be that during

FAME-09 the aerosol was less oxidized and less hygroscopic. Difference in instrumentation (different AMS units were used in the two campaigns) is another potential explanation. The average thermodenuded CE was estimated at 0.58 ± 0.14 and generally was equal or lower than the ambient CE. The average organic density of the ambient organic aerosol was estimated at $1.14 \pm 0.36 \text{ g cm}^{-3}$ while the thermodenuded at $1.06 \pm 0.34 \text{ g cm}^{-3}$.

In Chapter 5 the estimated CE's and organic densities for both the ambient and thermodenuded aerosol from FAME-08 are used as post-corrections in order to avoid the underestimation the OA volatility. We first evaluated the validity of this approach and then used the organic information from the AMS to calculate the evaporated organic fraction as a function of time and temperature for the FAME-08 data. The OA during the summer was quite uniform and highly oxidized due to the photochemistry. Using a multi-component organic aerosol evaporation model and the volatility-basis set we found that the organic aerosol during FAME-2008 is more than one order of magnitude less volatile than laboratory-generated α -pinene SOA.

Except for the organics the inorganic aerosol compounds play also important role in atmospheric chemistry. In Chapter 6 we modify the existing technique of SJAC in order to measure both particulate and gaseous phase of the main inorganic species, using alternatively a denuded and an undenuded sampling line. The first ambient tests at the Chemical Engineering Institute in Patra are promising. We were able to measure gas NH_3 concentrations from 4 to 80 ppb. This is consistent with the fact that the sampling area is agricultural, with a number of ammonia sources (e.g. animal waste, emissions from soil, etc.). We evaluated our results by comparing them with the predictions of the thermodynamic model ISORROPIA and for ammonia the agreement was very good. According to ISORROPIA the predicted nitric acid was at

very low concentrations (below 1 ppb). For predicted values of nitric acid below 0.5 ppb the measured nitric acid was sometimes negative, which implies that our system's detection limit for nitric acid is 0.5 ppb. For a better evaluation of nitric acid measurements, an urban location with higher NO_x and thus higher nitric acid levels is required.

Appendix A

Σύνοψη Διδακτορικής Διατριβής

Α1 ΠΕΡΙΛΗΨΗ

Τα αεροζόλ είναι σωματίδια που αιωρούνται στην ατμόσφαιρα και έχουν μέγεθος από 1nm μέχρι 50 μm. Περιέχουν μη πτητικές και ημιπτητικές ενώσεις και αποτελούνται κυρίως από θειικά, νιτρικά και αμμωνιακά άλατα, σκόνη, νερό, μέταλλα, και οργανικές ενώσεις. Τα ατμοσφαιρικά σωματίδια διαχωρίζονται σε πρωτογενή και δευτερογενή. Τα πρωτογενή εκπέμπονται κατευθείαν στην ατμόσφαιρα ενώ τα δευτερογενή είναι προϊόντα αντιδράσεων αέριων ρύπων και οργανικών πτητικών ενώσεων (VOCs) βιογενών αλλά και ανθρωπογενών, τα οποία είναι χαμηλής πτητικότητας και μεταφέρονται στην σωματιδιακή φάση. Όμως σε παγκόσμια κλίμακα, οι εκπομπές των βιογενών VOCs είναι κατά πολύ υψηλότερες από των ανθρωπογενών [1,2,3]. Οι κυριότερες από αυτές τις ενώσεις είναι το α-πινένιο, το β-πινένιο και το λεμονένιο. Για αυτό το λόγο η μελέτη των φυσικών και χημικών ιδιοτήτων των δευτερογενών οργανικών σωματιδίων που προέρχονται από τις παραπάνω ενώσεις έχει ιδιαίτερη σημασία. Ένα σημαντικό ποσοστό της μάζας των ατμοσφαιρικών σωματιδίων είναι ημιπτητικές ενώσεις. Αυτό σημαίνει ότι κάποιες ενώσεις μεταφέρονται συνεχώς μεταξύ αέριας και σωματιδιακής κατάστασης. Οι οργανικές ενώσεις που εμπεριέχονται στα σωματίδια είναι χιλιάδες (αλκάνια, αλκένια, αλδεΐδες, οργανικά οξέα, κετόνες, αρωματικές κυκλικές ενώσεις, πολυκυκλικές αρωματικές ενώσεις) και μόνο το 10-20% είναι σήμερα ανιχνεύσιμο και έτσι λίγα πράγματα είναι γνωστά.

Για το διαχωρισμό των συστατικών διαφορετικής πτητικότητας χρησιμοποιήθηκε ένας θερμικός απογυμνωτής σε κατάλληλες θερμοκρασίες. Εν συνεχεία το φάσμα μάζας αναλύθηκε σε 3 φάσματα ανάλογα με τη πτητικότητα με

χρήση φασματομετρίας μάζας αεροζόλ (Aerosol Mass Spectrometry, AMS). Η εύρεση της πυκνότητας των οργανικών σωματιδίων είναι επίσης δύσκολη. Ένας αλγόριθμος, ο οποίος συνδυάζει κατανομές μάζας και όγκου από μετρήσεις σε πραγματικό χρόνο, αναπτύχθηκε για την εύρεση της πυκνότητας των δευτερογενών οργανικών σωματιδίων. Στη συνέχεια εφαρμόστηκε σε πειράματα οζονόλυσης α-πινενίου, β-πινενίου και λεμονένιου σε περιβαλλοντικό θάλαμο με χρήση του AMS και σάρωση της κινητικότητας των σωματιδίων σε ηλεκτρικό πεδίο (Scanning Mobility Particle Sizer, SMPS). Η πυκνότητα των δευτερογενών οργανικών σωματιδίων υπολογίστηκε στο εύρος 1.4-1.65 g cm⁻³. Ο αλγόριθμος αυτός μπορεί επίσης να υπολογίσει και την ικανότητα συλλογής (CE) του AMS. Σε μετρήσεις πεδίου που πραγματοποιήθηκαν στη Κρήτη (FAME-08) μεταξύ των άλλων χρησιμοποιήθηκαν τα όργανα: AMS, SMPS, θερμικός απογυμνωτής και δειγματοληψία υγροποιημένων σωματιδίων. Ο παραπάνω αλγόριθμος εφαρμόστηκε για τον υπολογισμό της πυκνότητας των οργανικών σωματιδίων και της CE του AMS σε δείγματα κατευθείαν από την ατμόσφαιρα και σε δείγματα αφού είχαν περάσει από τον θερμικό απογυμνωτή. Η μέση πυκνότητα των οργανικών για τα δείγματα από την ατμόσφαιρα υπολογίστηκε στα 1.35±0.22 g cm⁻³ και για τα δείγματα μετά τον θερμικό απογυμνωτή 1.27±0.28 g cm⁻³. Η μέση CE αντίστοιχα εκτιμήθηκε στα 0.85±0.08 και 0.76±0.09. Οι τιμές αυτές χρησιμοποιήθηκαν ως διορθώσεις για τον υπολογισμό της κατανομής της πτητικότητας των οργανικών σωματιδίων.

A2 ΕΙΣΑΓΩΓΗ

Τα ατμοσφαιρικά σωματίδια σε αυξημένες συγκεντρώσεις προκαλούν προβλήματα υγείας στους ανθρώπους και μειωμένη ορατότητα [4]. Επίσης κατέχουν σημαντικό ρόλο στην ατμοσφαιρική χημεία καθώς αποτελούν πυρήνες συμπύκνωσης για το νερό με αποτέλεσμα τη δημιουργία των σύννεφων. Παράλληλα επηρεάζουν και το ενεργειακό ισοζύγιο του πλανήτη ψύχοντάς τον αφού αντανακλούν ηλιακή ακτινοβολία πίσω στο διάστημα [5].

Μέχρι πριν από μερικά χρόνια η χημική ανάλυση των ατμοσφαιρικών σωματιδίων γινόταν με συλλογή τους σε φίλτρα και ανάλυση τους στο εργαστήριο. Όμως η χημική περιπλοκότητα και η ασταθής τους φύση έστρεψε την έρευνα σε τεχνικές μετρήσεων πραγματικού χρόνου, χωρίς να είναι απαραίτητη η συλλογή, η αποθήκευση και η μεταφορά δειγμάτων. Επίσης με μετρήσεις σε πραγματικό χρόνο λαμβάνονται περισσότερα δείγματα. Παράλληλα, απαραίτητη είναι και η μελέτη των φυσικών ιδιοτήτων όπως οι κατανομές αριθμού, και όγκου (και επομένως και η συγκέντρωση του αριθμού και του όγκου στην ατμόσφαιρα).

Η διδακτορική αυτή εργασία έχει στηριχθεί σε μεγάλο βαθμό στη χρήση φασματομετρίας μάζας αεροζόλ χρησιμοποιώντας το AMS της εταιρείας Aerodyne [6,7,8,9,10]. Το AMS μετράει σε πραγματικό χρόνο τη χημική σύσταση των σωματιδίων, τη μάζα των επιμέρους συστατικών τους και τις κατανομές μάζας αυτών ως συνάρτηση της αεροδυναμικής διαμέτρου υπό κενό. Το όργανο αυτό έχει χρησιμοποιηθεί σε πολλές μετρήσεις πεδίου όπως για παράδειγμα στο Εδιμβούργο και στο Μάντσεστερ (2000-2001), στη Νέα Υόρκη (2001), στο Πίτσμπουργκ (2002), στη Πόλη του Μεξικού (2003) και αλλά και σε εργαστηριακά πειράματα [11, 7, 12].

Έτσι το AMS σήμερα θεωρείται ένα από τα πιο χρήσιμα όργανα. Σε συνδυασμούς με άλλα όργανα όπως το SMPS, το SJAC και τον θερμικό απογυμνωτή μπορεί να δώσει πολύτιμες πληροφορίες για τις χημικές και φυσικές ιδιότητες των ατμοσφαιρικών σωματιδίων.

A3 ΠΡΟΣΔΙΟΡΙΣΜΟΣ ΦΑΣΜΑΤΩΝ ΜΑΖΑΣ ΤΩΝ ΒΙΟΓΕΝΩΝ ΟΡΓΑΝΙΚΩΝ ΣΩΜΑΤΙΔΙΩΝ ΣΕ ΦΑΣΜΑΤΑ ΜΑΖΑΣ ΧΑΜΗΛΗΣ, ΜΕΤΡΙΑΣ ΚΑΙ ΥΨΗΛΗΣ ΠΤΗΤΙΚΟΤΗΤΑΣ

Τα δευτερογενή οργανικά σωματίδια (secondary organic aerosol, SOA) αποτελούνται από ενώσεις με μεγάλο εύρος πτητικοτήτων και η συγκέντρωσή τους στο περιβάλλον είναι ευαίσθητη σε αυτή την κατανομή πτητικότητας. Πρόσφατες έρευνες έδειξαν ότι το φάσμα ενός φασματογράφου μάζας σωματιδίων (Aerodyne Aerosol Mass Spectrometer, AMS), μπορεί να διαχωριστεί σε οργανικά σωματίδια υδρογονανθράκων (hydrocarbon-like organic aerosol, HOA) και σε οξυγονωμένα οργανικά σωματίδια (oxygenated organic aerosol, OOA) [13]. Από τις μελέτες αυτές προέκυψε ότι το φάσμα μάζας των OOA είναι παρόμοιο με αυτό των γηρασμένων οργανικών σωματιδίων σε απομακρυσμένες περιοχές, αλλά αρκετά διαφορετικό από το φάσμα μάζας των SOA όπως προκύπτει από πειραματικές μετρήσεις σε περιβαλλοντικό θάλαμο. Το φάσμα των OOA χαρακτηρίζεται από το m/z 44, ενώ αυτό των εργαστηριακών SOA που προέρχονται από τις πρόδρομες ενώσεις των α -πινενίου, β -πινενίου, λεμονενίου και β -καριοφυλλενίου έχει μεγαλύτερο σήμα στο m/z 43 σε σχέση με το 44. Μέρος αυτής της διαφοράς πιθανόν οφείλεται στην εξάρτηση της σύστασης των SOA από την συγκέντρωση των οργανικών σωματιδίων. Έτσι

υψηλές συγκεντρώσεις πρόδρομων ενώσεων οδηγούν σε υψηλότερες συγκεντρώσεις πτητικών ειδών στα παραγόμενα SOA, ενώ σε χαμηλότερες συγκεντρώσεις η σύσταση των SOA κυριαρχείται από συστατικά χαμηλότερης πτητικότητας.

Σε αυτήν την μελέτη πραγματοποιήθηκαν πειράματα οζονόλυσης, α-πινενίου, β-πινενίου, λεμονενίου και β-καριοφυλλενίου σε μέτρια επίπεδα συγκεντρώσεων. Χρησιμοποιώντας έναν θερμικό απογυμνωτή τα περισσότερα πτητικά συστατικά των SOA απομακρύνονται, επιτυγχάνοντας έτσι ακόμα χαμηλότερες συγκεντρώσεις SOA. Το κλάσμα των λιγότερο πτητικών ειδών που απέμεινε στην έξοδο του θερμικού απογυμνωτή χαρακτηριζόταν έπειτα από το AMS. Στη συνέχεια χρησιμοποιήσαμε ένα μοντέλο προσομοίωσης του περιβαλλοντικού θαλάμου, ένα μοντέλο προσομοίωσης του θερμικού απογυμνωτή και την κατανομή πτητικότητας (volatility basis-set). Με αυτά τα μέσα αναλύσαμε το φάσμα μάζας του AMS για κάθε πείραμα και για κάθε πρόδρομη ένωση σε φάσμα χαμηλής, μεσαίας και υψηλής πτητικότητας.

A 3.1 MONTEΛΑ ΓΙΑ ΤΗΝ ΑΝΑΛΥΣΗ ΔΕΔΟΜΕΝΩΝ

Για την ανάλυση μας χρειαζόμαστε τη σύσταση των SOA καθώς αυτά εξέρχονται από τον θερμικό απογυμνωτή στις διάφορες θερμοκρασίες. Για να υπολογίσουμε αυτή τη σύσταση χρησιμοποιούμε 2 μοντέλα. Πρώτα χρησιμοποιώντας το volatility basis-set [14] υπολογίζεται η σύσταση των αεροζόλ που βγαίνουν από τον περιβαλλοντικό θάλαμο και εισέρχονται στον θερμικό απογυμνωτή. Στη συνέχεια προσομοιώνουμε την εξάτμιση των οργανικών αεροζόλ μέσα στο θερμικό απογυμνωτή σύμφωνα με το μοντέλο των Lee et al. [15] και υπολογίζουμε τη σύσταση του αεροζόλ που έχει απομείνει αφού περάσει από τον θερμικό απογυμνωτή

ως συνάρτηση της πτητικότητας. Τέλος το φάσμα μάζας του AMS αναλύεται σε 3 φάσματα ανάλογα με τη πτητικότητα.

A 3.2 ΑΠΟΤΕΛΕΣΜΑΤΑ-ΣΥΖΗΤΗΣΗ

Το κλάσμα μάζας, MFR, (μετρημένο από το AMS) που απομένει αφού το αεροζόλ περάσει από τον θερμικό απογυμνωτή συγκρίθηκε με το κλάσμα όγκου, VFR, (μετρημένο από το SMPS). Η συμφωνία των δύο οργάνων είναι πολύ καλή με $R^2=0.983$.

Επίσης μελετήθηκε η συμπεριφορά του m/z 44, η οποία είναι χαρακτηριστική για το CO_2^+ , και αυτή του m/z 43, χαρακτηριστική των φρέσκων σωματιδίων, σε συνάρτηση με το κλάσμα μάζας MFR. Καθώς η θερμοκρασία μέσα στον θερμικό απογυμνωτή αυξάνεται και άρα το κλάσμα μάζας που απομένει μειώνεται, το κλάσμα του σήματος του m/z 44 αυξάνεται (Εικόνα 1) ενώ του 43 μειώνεται. Αυτό είναι μία ένδειξη ότι το λιγότερο πτητικό αεροζόλ, το οποίο και κυριαρχεί στις συγκεντρώσεις περιβάλλοντος, είναι περισσότερο οξυγονωμένο. Επίσης το φάσμα μάζας από το AMS εξαρτάται από τη συγκέντρωση των SOA.

Το φάσμα μάζας κάθε ένωσης αναλύθηκε σε 3 επιμέρους φάσματα ανάλογα με την πτητικότητά τους. Το φάσμα των λιγότερο πτητικών ενώσεων (με συγκέντρωση κορεσμού $C^*=1 \mu\text{g m}^{-3}$) του β-πινενίου και του α-πινενίου μοιάζει με εκείνο των οξυγονωμένων που λαμβάνουμε από το περιβάλλον (OOA), ενώ του λεμονενίου όχι (Εικόνα 2).

Εικόνα 1. Το κλάσμα του σήματος του m/z 44 σε σχέση με το κλάσμα μάζας MFR μετά τον θερμικό απογυμνωτή για 100 ppb πρόδρομης ένωσης σε συνθήκες χαμηλής συγκέντρωσης NO_x και σχετικής υγρασίας. Το κλάσμα του σήματος του m/z 44 (CO_2^+) αυξάνεται καθώς η θερμοκρασία αυξάνεται και το κλάσμα μάζας που απομένει μειώνεται. Καθώς η πτητικότητα μειώνεται το αεροζόλ περιέχει μεγαλύτερο ποσοστό οξειδωμένων συστατικών.

Εικόνα 2. Το φάσμα μάζας των συστατικών με τη χαμηλότερη πτητικότητα (a) για το β -πινένιο, (b) το α -πινένιο, (c) το λεμονένιο και (d) των οξυγονωμένων από το Πίτσμπουργκ.

A4 ΑΝΑΠΤΥΞΗ ΑΛΓΟΡΙΘΜΟΥ ΓΙΑ ΤΗ ΣΥΓΚΡΙΣΗ ΔΕΔΟΜΕΝΩΝ ΑΠΟ AMS ΚΑΙ SMPS: ΥΠΟΛΟΓΙΣΜΟΣ ΠΥΚΝΟΤΗΤΑΣ ΔΕΥΤΕΡΟΓΕΝΩΝ ΟΡΓΑΝΙΚΩΝ ΣΩΜΑΤΙΔΙΩΝ

Παρά την όλη πρόοδο στην επιστήμη των ατμοσφαιρικών αεροζόλ δεν υπάρχει ακόμα κάποια γενική μέθοδος για τον υπολογισμό της πυκνότητας των οργανικών συστατικών τους για περιπτώσεις όπου η χημική σύσταση εξαρτάται από το μέγεθος των σωματιδίων. Στην εργασία αυτή παρουσιάζεται ένας νέος αλγόριθμος για τον υπολογισμό της πυκνότητας των οργανικών αεροζόλ σε σωματίδια που περιέχουν οργανική και ανόργανη ύλη χρησιμοποιώντας δεδομένα από τον φασματογράφο μάζας για σωματίδια (AMS) και μετρητή κατανομής με σάρωση ηλεκτρικής κινητικότητας (SMPS). Ο παραπάνω αλγόριθμος υπολογίζει ταυτόχρονα και την ικανότητα συλλογής (Collection Efficiency, CE) του AMS. Η μέθοδος αφορά σωματίδια των οποίων η χημική σύσταση εξαρτάται από το μέγεθος τους και εφαρμόστηκε σε δευτερογενή οργανικά σωματίδια (SOA) που δημιουργήθηκαν με οζονόλυση α-πινενίου, β-πινενίου και λεμονένιου. Τα πειράματά μας αφορούν χαμηλές συγκεντρώσεις δευτερογενών οργανικών ενώσεων, κοντά στις συνθήκες περιβάλλοντος και άρα απαιτείται η παρουσία ανόργανων σωματιδίων [16], συνήθως θειικού αμμωνίου.

A4.1 ΑΛΓΟΡΙΘΜΟΣ

Η σχέση που συνδέει την κατανομή μάζας και όγκου είναι:

$$\frac{dV}{d \log D_m} = \frac{d(M / \rho)}{d \log D_m} \frac{1}{CE} \quad (1)$$

όπου V είναι ο όγκος των σωματιδίων, M η μάζα τους, D_m η κινητική διάμετρος και ρ η ολική πυκνότητα των σωματιδίων. Υποθέτοντας προσθετικότητα του όγκου η πυκνότητα ρ δίνεται από:

$$\rho = x_{a/s} \rho_{a/s} + x_{SOA} \rho_{SOA} \quad (2)$$

όπου $x_{a/s}$ είναι το κλάσμα μάζας του θειικού αμμωνίου, x_{SOA} είναι το κλάσμα μάζας των δευτερογενών οργανικών σωματιδίων, $\rho_{a/s}$ είναι η πυκνότητα του θειικού αμμωνίου (1.77 g cm^{-3}) και ρ_{SOA} είναι η άγνωστη πυκνότητα των δευτερογενών οργανικών σωματιδίων.

Για σφαιρικά σωματίδια η εξίσωση μεταξύ κινητικής διαμέτρου (D_m) και αεροδυναμικής διαμέτρου υπό κενό (D_{va}) είναι [17]:

$$D_m = \frac{D_{va}}{\rho} \rho_o \quad (3)$$

όπου ρ_o είναι η μοναδιαία πυκνότητα (1 g cm^{-3}).

Για ανάμικτα ανόργανα-οργανικά σωματίδια η χημική σύσταση δεν είναι σταθερή με τη διάμετρο και έτσι η πυκνότητα εξαρτάται από το μέγεθος. Η πυκνότητα των δευτερογενών οργανικών σωματιδίων μπορεί να υπολογιστεί από τον παρακάτω αλγόριθμο, ο οποίος βασίζεται στον υπολογισμό της κατανομής όγκου ως συνάρτηση της κινητικής διαμέτρου χρησιμοποιώντας δεδομένα από το AMS, δηλαδή τη κατανομή μάζας ως συνάρτηση της αεροδυναμικής διαμέτρου υπό κενό:

- (1) Το εύρος της αεροδυναμικής διαμέτρου χωρίζεται σε 6 με 8 τμήματα.
- (2) Για κάθε τμήμα υπολογίζεται η μέση τιμή του κλάσματος μάζας του θειικού αμμωνίου ($x_{a/s}$) και του κλάσματος μάζας των δευτερογενών οργανικών σωματιδίων

(x_{SOA}) χρησιμοποιώντας πειραματικά δεδομένα του AMS. Αυτές οι τιμές αντιστοιχούν στη μέση αεροδυναμική διάμετρο υπό κενό του κάθε τμήματος.

(3) Γίνεται μία αρχική πρόβλεψη για τη πυκνότητα των δευτερογενών οργανικών σωματιδίων π.χ. 1 g cm^{-3} .

(4) Μέσω της (2) υπολογίζεται η φαινομενική πυκνότητα για κάθε τμήμα.

(5) Η φαινομενική πυκνότητα υπολογίζεται ως συνάρτηση της μέσης αεροδυναμικής διαμέτρου χρησιμοποιώντας 2 γραμμικές εξισώσεις με τη παρακάτω μορφή:

$$\rho = e + fD_{va} \quad (4)$$

Συνδυάζοντας τις εξισώσεις (1), (2), (3) και (4) προκύπτει η επιθυμητή εξίσωση για τον υπολογισμό της κατανομής όγκου βασισμένη σε δεδομένα του AMS:

$$\frac{dV}{d \log D_m} = \left(\frac{1}{e} \frac{dM}{d \log D_{va}} - M(D_{va}) \frac{e}{f} \frac{D_{va}}{\rho} \ln 10 \right) \frac{1}{CE} \quad (5)$$

Έπειτα συγκρίνουμε τα αποτελέσματα του αλγόριθμου με τα πειραματικά αποτελέσματα του SMPS για περίπου 10 χρονικές στιγμές σε κάθε πείραμα. Για να επιλέξουμε την καλύτερη καμπύλη και επομένως την καταλληλότερη πυκνότητα των δευτερογενών οργανικών σωματιδίων χρησιμοποιούμε την εξίσωση (6):

$$Error \text{ Score}_t = \frac{\sum_i \sqrt{(a_{it} - b_{it})^2}}{\sum_i \sqrt{a_{it}^2}} \quad (6)$$

όπου a_{it} είναι η τιμή της κατανομής όγκου από το SMPS σε διάμετρο i για το χρόνο t και b_{it} είναι η αντίστοιχη τιμή της κατανομής όγκου υπολογισμένη από το AMS για την ίδια διάμετρο i και στον ίδιο χρόνο t (Εικόνα 3).

Εικόνα 3: Μέσο σφάλμα ως συνάρτηση της πυκνότητας των δευτερογενών οργανικών σωματιδίων και της CE.

Διαλέγουμε τις τιμές της πυκνότητας και της CE οι οποίες ελαχιστοποιούν το σφάλμα (εξίσωση 6).

A4.2 ΑΠΟΤΕΛΕΣΜΑΤΑ-ΣΥΖΗΤΗΣΗ

Στα πειράματα συμπύκνωσης για το α-πινένιο η μέση πυκνότητα των δευτερογενών οργανικών σωματιδίων εκτιμήθηκε στα $1.41 \pm 0.06 \text{ g cm}^{-3}$, για το β-πινένιο στα $1.45 \pm 0.14 \text{ g cm}^{-3}$ και για το λεμονένιο στα $1.49 \pm 0.24 \text{ g cm}^{-3}$. Στα πειράματα πυρηνογένεσης η μέση πυκνότητα του α-πινενίου κυμαίνεται στα $1.5 \pm 0.06 \text{ g cm}^{-3}$, του β-πινενίου στα $1.46 \pm 0.1 \text{ g cm}^{-3}$ και του λεμονένιου στα $1.56 \pm 0.1 \text{ g cm}^{-3}$. Σε δύο μόνο περιπτώσεις πυρηνογένεσης εκτιμήθηκαν πυκνότητες $1.00 \pm 0.02 \text{ g cm}^{-3}$. Η υψηλή τιμή της πυκνότητας ($1.4 - 1.55 \text{ g cm}^{-3}$) υποδηλώνει ότι τα σχηματιζόμενα δευτερογενή οργανικά σωματίδια είναι μάλλον σε στερεά ή κερώδη κατάσταση. Η υψηλή αυτή τιμή της πυκνότητας των οργανικών σημαίνει ότι οι συγκεντρώσεις μάζας αυτών των σωματιδίων που υπολογίζονται από τα τρισδιάστατα

μοντέλα ατμοσφαιρικής ρύπανσης είναι λανθασμένες γιατί έχουν βασιστεί σε μετρήσεις όγκου και έχουν υποθέσει πυκνότητα 1 g cm^{-3} .

A5 ΜΕΤΡΗΣΕΙΣ ΧΗΜΙΚΗΣ ΣΥΣΤΑΣΤΗΣ ΤΩΝ ΟΡΓΑΝΙΚΩΝ ΣΩΜΑΤΙΔΙΩΝ ΣΕ ΜΕΤΡΗΣΕΙΣ ΠΕΔΙΟΥ (FAME 2008-2009) ΣΤΗ ΦΙΝΟΚΑΛΙΑ: ΥΠΟΛΟΓΙΣΜΟΣ ΙΚΑΝΟΤΗΤΑΣ ΣΥΛΛΟΓΗΣ ΤΟΥ AMS ΚΑΙ ΤΗΣ ΟΡΓΑΝΙΚΗΣ ΠΥΚΝΟΤΗΤΑΣ

Κατά τη διάρκεια του πειράματος Finokalia Aerosol Measurement Experiment, στις αρχές καλοκαιριού (FAME-08) και του χειμώνα (FAME-09) πραγματοποιήθηκαν εντατικές μετρήσεις ατμοσφαιρικών σωματιδίων. Και τα 2 πειράματα ήταν μέρος ενός γενικότερου Ευρωπαϊκού προγράμματος μετρήσεων σε πεδίο. Ο σταθμός της Φινοκαλιάς βρίσκεται σε ένα απομονωμένο μέρος κοντά στη θάλασσα στα βορειοανατολικά της Κρήτης. Είναι μακριά από ανθρωπογενείς πηγές ρύπων και αυτό μας επιτρέπει τη μελέτη γηρασμένων οργανικών σωματιδίων τα οποία έρχονται από όλες τις κατευθύνσεις. Για τη μέτρηση των σωματιδίων με διάμετρο μικρότερη από $1 \mu\text{m}$ (PM_{10}) χρησιμοποιήθηκε το AMS. Στο FAME-08 το μεγαλύτερο μέρος των PM_{10} ήταν θειικό αμμώνιο και όξινο θειικό αμμώνιο και μετά ακολουθούσαν τα οργανικά με σχεδόν καθόλου νιτρικά. Το φάσμα των οργανικών άλλαζε λίγο σε σχέση με την περιοχή από την οποία προέρχονταν. Στο FAME-09 τα θειικά και τα οργανικά είχαν σχεδόν ίσες συγκεντρώσεις, ενώ τα νιτρικά ήταν επίσης πολύ χαμηλά. Οι συγκεντρώσεις των αεροζόλ το καλοκαίρι (FAME-08) ήταν σχεδόν 3 φορές πιο μεγάλες σε σχέση με αυτές το χειμώνα (FAME-09) [18]. Ένας θερμικός απογυμνωτής [19] συνδυασμένος με το AMS και ένα SMPS χρησιμοποιήθηκε για το προσδιορισμό

της πτητικότητας των οργανικών σωματιδίων. Χρησιμοποιώντας τον αλγόριθμο των Kostenidou et al., [20] υπολογίστηκε η πυκνότητα των οργανικών σωματιδίων και η CE του AMS και για τα ατμοσφαιρικά (BP) αλλά και για τα δείγματα από τον θερμικό απογυμνωτή. (TD). Χρησιμοποιήσαμε αυτές τις τιμές για να διορθώσουμε τις μετρήσεις του AMS και συγκρίνοντας με άλλα όργανα (π.χ. φίλτρα, SJAC) η συσχέτιση ήταν αρκετά καλή.

A5.1 ΑΠΟΤΕΛΕΣΜΑΤΑ-ΣΥΖΗΤΗΣΗ

Το ποσοστό του νερού κατά τη διάρκεια του FAME-08 κυμαινόταν από 0 μέχρι 25%, ενώ στο FAME-09 0-50%. Έτσι πρέπει να συνυπολογιστούν και οι κατανομές του νερού στον αλγόριθμο για τον υπολογισμό της πυκνότητας των οργανικών και της CE.

A5.2 FAME-08

Η CE του AMS των ατμοσφαιρικών σωματιδίων υπολογίστηκε κατά μέσο όρο σε 0.85 ± 0.08 (Εικόνα 4). Αυτή η τιμή είναι μεγαλύτερη από αυτές που χρησιμοποιούν οι υπόλοιπες ομάδες σε μετρήσεις πεδίου. Αυτό μπορεί να οφείλεται στο γεγονός ότι σε άλλες μετρήσεις πεδίου το αεροζόλ ξηραίνεται πριν γίνει η δειγματοληψία και τα ξηρότερα σωματίδια αναπηδούν στον φούρνο εξάτμισης του AMS και η CE είναι μικρότερη. Επίσης στο FAME-08 το αεροζόλ ήταν ιδιαίτερο υγροσκοπικό καθώς καθώς τα οργανικά ήταν οξειδωμένα και καθώς η ανόργανη μάζα ήταν μεγαλύτερη από την οργανική. Η CE, για τα σωματίδια που πέρασαν από τον θερμικό απογυμνωτή, βρέθηκε 10-20% χαμηλότερη και κατά μέσο όρο 0.76 ± 0.09 .

Αυτό μάλλον σημαίνει ότι η εξάτμιση του νερού μέσα στο θερμικό απογυμνωτή αυξάνει τη πιθανότητα αναπήδησης των σωματιδίων πάνω στο φούρνο εξάτμισης και τελικά μειώνει την CE.

Εικόνα 4: Η CE του AMS για τα ατμοσφαιρικά σωματίδια για το FAME-08. Οι μωβ σκιές είναι οι λύσεις που δίνουν σφάλμα μέσα σε εύρος 10% από το ελάχιστο σφάλμα.

Η πυκνότητα των ατμοσφαιρικών οργανικών σωματιδίων κατά μέσο όρο υπολογίστηκε στα $1.35 \pm 0.22 \text{ g cm}^{-3}$ (Εικόνα 5). Δε βρέθηκε κάποια συσχέτιση μεταξύ της οργανικής πυκνότητας και της προέλευσης των σωματιδίων. Οι διακυμάνσεις που παρατηρούνται ίσως να οφείλονται στη διαφορετική συνεισφορά του νερού. Βρέθηκε ότι σε χαμηλότερες συγκεντρώσεις νερού η οργανική πυκνότητα είναι μεγαλύτερη. Ένας λόγος για αυτό μπορεί να είναι ότι σε μεγαλύτερες ποσότητες νερού μεγαλύτερο ποσό από τα οξυγονωμένα οργανικά σωματίδια μπορούν να διαλύονται, αντί να είναι πακτωμένα το ένα κοντά στο άλλο σε στερεή κατάσταση και αυτό αυξάνει τον όγκο που καταλαμβάνουν μειώνοντας τη πυκνότητα. Η μέση πυκνότητα των οργανικών σωματιδίων μετά τον θερμικό απογυμνωτή υπολογίστηκε στα $1.27 \pm 0.28 \text{ g cm}^{-3}$ και στατιστικά είναι ίδια με την πυκνότητα των ατμοσφαιρικών οργανικών.

Εικόνα 4: Η πυκνότητα των ατμοσφαιρικών οργανικών σωματιδίων για το FAME-08. Οι πράσινες σκιές είναι οι λύσεις που δίνουν σφάλμα μέσα σε εύρος 10% από το ελάχιστο σφάλμα.

Εφαρμόζοντας την υπολογισμένη από τον αλγόριθμο CE των ατμοσφαιρικών σωματιδίων στις μετρήσεις του AMS υπολογίσαμε τις πραγματικές συγκεντρώσεις των PM_{10} (Εικόνα 5). Συγκρίνοντας συγκεντρώσεις θεικών και αμμωνίου από φίλτρα PM_{10} η συμφωνία ήταν αρκετά καλή ($R^2 = 0.95$, και $R^2 = 0.84$, αντίστοιχα).

Εικόνα 5: Οι χρονοσειρές για τα θειικά, νιτρικά και οργανικά σωματίδια μετά τις διορθώσεις από τον αλγόριθμο για την CE των ατμοσφαιρικών σωματιδίων για το FAME-08. Η μέση συνολική συγκέντρωση ήταν $9 \mu g m^{-3}$.

A 5.3 FAME-09

Χρησιμοποιώντας και πάλι τον αλγόριθμο που συνδυάζει δεδομένα από το AMS και το SMPS η CE του AMS για τα ατμοσφαιρικά αεροζόλ υπολογίστηκε κατά μέσο όρο 0.64 ± 0.13 (Εικόνα 6). Το γεγονός ότι είναι μικρότερη από αυτή του καλοκαιριού υπονοεί ότι τα σωματίδια είχαν διαφορετικές ιδιότητες. Ο λόγος των οργανικών προς τα θειικά είναι περίπου ένα για το FAME-09 ενώ για το FAME-08 περίπου 0.5. Έτσι το κλάσμα των περισσότερο υγροσκοπικών ενώσεων όπως τα θειικά ήταν μικρότερο το χειμώνα. Επίσης οι μικρότερες συγκεντρώσεις OH κατά τη διάρκεια του χειμώνα συνέβαλλαν στη δημιουργία λιγότερο γηρασμένου και επομένως λιγότερο υγροσκοπικού αεροζόλ. Η CE των σωματιδίων μετά τον θερμικό απογυμνωτή υπολογίστηκε κατά μέσο όρο 0.58 ± 0.14 (Εικόνα 6) και γενικά ήταν μικρότερη η ίση από των ατμοσφαιρικών σωματιδίων. Η μέση οργανική πυκνότητα για τα ατμοσφαιρικά σωματίδια δειγмата βρέθηκε $1.14 \pm 0.36 \text{ g cm}^{-3}$ ενώ για αυτά που πέρασαν από τον θερμικό απογυμνωτή και εξατμίστηκαν μερικά $1.06 \pm 0.34 \text{ g cm}^{-3}$.

Εικόνα 6: Η CE του AMS για τα ατμοσφαιρικά σωματίδια και για τα σωματίδια που πέρασαν από τον θερμικό απογυμνωτή για το FAME-09.

Α6 ΜΕΤΡΗΣΕΙΣ ΠΗΤΗΤΙΚΟΤΗΤΑΣ ΤΩΝ ΟΡΓΑΝΙΚΩΝ ΣΩΜΑΤΙΔΙΩΝ ΣΤΗ ΦΙΝΟΚΑΛΙΑ

Κατά τη διάρκεια του FAME-08 μεταξύ των άλλων χρησιμοποιήθηκε ένας θερμικός απογυμνωτής, ένα AMS και ένα SMPS για μετρήσεις πτητικότητας. Όπως συζητήθηκε προηγουμένως με τη βοήθεια του αλγορίθμου που συνδυάζει τις κατανομές μάζας από το AMS και τις κατανομές όγκου από το SMPS υπολογίστηκε η CE και η πυκνότητα των BP και TD οργανικών σωματιδίων. Χρησιμοποιήσαμε αυτά τα δεδομένα στον υπολογισμό της πτητικότητας των οργανικών αεροζόλ.

Α6.1 ΤΕΣΤ ΤΟΥ ΑΛΓΟΡΙΘΜΟΥ

Για να εκτιμήσουμε πόσο καλά λειτουργεί ο αλγόριθμος υπολογίσαμε τις κατανομές αριθμού και όγκου των σωματιδίων που πέρασαν από τον θερμικό απογυμνωτή, χρησιμοποιώντας τις αντίστοιχες κατανομές των ατμοσφαιρικών σωματιδίων, τις συγκεντρώσεις των συστατικών που μετρήθηκαν από το AMS των ατμοσφαιρικών σωματιδίων και αυτών που πέρασαν από τον θερμικό απογυμνωτή, την πυκνότητα οργανικών των ατμοσφαιρικών σωματιδίων καθώς και αυτών που πέρασαν από τον θερμικό απογυμνωτή, την CE των ατμοσφαιρικών σωματιδίων και αυτών που πέρασαν από τον θερμικό απογυμνωτή και τις εκτιμώμενες απώλειες αριθμού σωματιδίων.

Το κλάσμα όγκου που απομένει μετά τον θερμικό απογυμνωτή (VFR) μπορεί να υπολογιστεί από την εξίσωση:

$$VFR = \left[\frac{[OA]_{TD} / \rho_{org_TD} + [Sulfates]_{TD} / \rho_{a/s} + [Water]_{TD} / \rho_w}{[OA]_{amb} / \rho_{org_amb} + [Sulfates]_{amb} / \rho_{a/s} + [Water]_{amb} / \rho_w} \right] \cdot \frac{CE_{amb}}{CE_{TD}} \cdot \frac{1}{1 - f_N} \quad (7)$$

όπου ο δείκτης TD δηλώνει ένα δείγμα που πέρασε από τον θερμικό απογυμνωτή, amb ένα δείγμα κατευθείαν από την ατμόσφαιρα. $[OA]$ είναι η συγκέντρωση μάζας των οργανικών αεροζόλ, $[Sulfates]$ είναι συγκέντρωση μάζας των σωματιδίων θειικού και όξινου θειικού αμμωνίου, $[Water]$ είναι η συγκέντρωση μάζας του νερού, ρ_{org} είναι η πυκνότητα των οργανικών σωματιδίων και υπολογίζεται από τον αλγόριθμο των Kostenidou et al. [20], $\rho_{a/s}$ είναι η πυκνότητα του θειικού αμμωνίου, ρ_w είναι η πυκνότητα του νερού, CE_{amb} είναι η CE του AMS για τα ατμοσφαιρικά αεροζόλ, CE_{TD} είναι η CE του AMS για τα σωματίδια που πέρασαν από τον θερμικό απογυμνωτή και f_N είναι το κλάσμα των απωλειών του αριθμού σωματιδίων μέσα στον θερμικό απογυμνωτή βασιζόμενος σε κατανομές αριθμού των ατμοσφαιρικών σωματιδίων και αυτών που πέρασαν από τον θερμικό απογυμνωτή.

Η διάμετρος ενός σωματιδίου που έχει περάσει από τον θερμικό απογυμνωτή, $D_{p,TD}$ δίνεται από τον τύπο:

$$D_{p,TD} = D_{p,amb} (VFR)^{\frac{1}{3}} \quad (8)$$

όπου $D_{p,amb}$ είναι η διάμετρος ενός ατμοσφαιρικού σωματιδίου. Στη συνέχεια μπορούμε να υπολογίσουμε την κατανομή αριθμού των σωματιδίων που πέρασαν από τον θερμικό απογυμνωτή, $n_n(D_{p,TD})$:

$$n_n(D_{p,TD}) = n_n(D_{p,amb}) \cdot \left(\frac{dD_{p,amb}}{dD_{p,TD}} \right) \cdot (1 - f_N) \quad (9)$$

όπου $n_n(D_{p,amb})$ είναι η κατανομή αριθμού των ατμοσφαιρικών σωματιδίων όπως τη μετράει το SMPS. Η κατανομή όγκου των σωματιδίων που πέρασαν από τον θερμικό απογυμνωτή μπορεί να γραφτεί, $n_v(D_{p,TD})$:

$$n_v(D_{p,TD}) = n_v(D_{p,amb}) \cdot \left(\frac{dD_{p,amb}}{dD_{p,TD}} \right) \cdot (1 - f_N) \quad (10)$$

όπου $n_v(D_{p,amb})$ είναι κατανομή όγκου των ατμοσφαιρικών σωματιδίων από το SMPS.

Στη συνέχεια συγκρίνουμε τις κατανομές αριθμού και όγκου των σωματιδίων που πέρασαν από τον θερμικό απογυμνωτή οι οποίες προκύπτουν από τις εξισώσεις (9) και (10) με τις πραγματικές κατανομές των σωματιδίων που πέρασαν από τον θερμικό απογυμνωτή οι οποίες μετρήθηκαν από το SMPS. Στην Εικόνα 7 φαίνεται ένα παράδειγμα. Καθ' όλη τη διάρκεια του FAME-08 οι κατανομές αυτές συμφωνούν πολύ καλά μεταξύ τους, που σημαίνει ότι ο αλγόριθμος για την εύρεση της CE και της οργανικής πυκνότητας είναι συνεπής.

Εικόνα 7: Κατανομές αριθμού και όγκου για BP και TD σωματίδια στις 1-2 π.μ. στις 2 Ιουνίου 2008. Η θερμοκρασία του θερμικού απογυμνωτή ήταν στους 106°C [21].

Α6.2 ΑΠΟΤΕΛΕΣΜΑΤΑ-ΣΥΖΗΤΗΣΗ

Στη συνέχεια χρησιμοποιώντας τις CE και την οργανική πυκνότητα που υπολογίστηκαν από τον αλγόριθμο των Kostenidou et al. [20] διορθώσαμε την συγκέντρωση των οργανικών σωματιδίων. Η εικόνα 8 δείχνει την επίδραση που έχουν αυτές οι διορθώσεις: οι αλλαγές της CE και της πυκνότητας των οργανικών κατά τη θέρμανση καθώς και οι απώλειες μέσα στον θερμικό απογυμνωτή οδηγούν σε ~20% υποεκτίμηση του κλάσματος μάζας που εξατμίζεται. Περαιτέρω επεξεργασία αυτών των δεδομένων και με τη βοήθεια του volatility basis-set οι Lee et al. [21] έδειξαν ότι τα οργανικά σωματίδια κατά τη διάρκεια του FAME-08 ήταν παραπάνω από μία τάξεις μεγέθους λιγότερο πτητικά σε σχέση με τα SOA που παράγονται από α-πινένιο στο εργαστήριο.

Εικόνα 8: Το κλάσμα μάζας που απομένει στην έξοδο του θερμικού απογυμνωτή ως συνάρτηση της θερμοκρασίας για μη διορθωμένα δεδομένα (μπλε ρόμβοι), για διορθωμένα δεδομένα (κόκκινα τρίγωνα) και για φρέσκα SOA α-πινενίου από πειράματα εργαστηρίου τις ίδιας περίπτωσης συγκέντρωσης ($10 \mu\text{g m}^{-3}$) και του ίδιου μεγέθους (250 nm) [21].

A7 ΤΡΟΠΟΠΟΙΗΣΗ ΤΗΣ ΜΕΘΟΔΟΥ ΔΕΙΓΜΑΤΟΛΗΨΙΑΣ ΥΓΡΟΠΟΙΗΜΕΝΩΝ ΣΩΜΑΤΙΔΙΩΝ ΓΙΑ ΜΕΤΡΗΣΕΙΣ ΣΩΜΑΤΙΔΙΑΚΗΣ ΚΑΙ ΑΕΡΙΑΣ ΦΑΣΗΣ

Για την ημι-συνεχή μέτρηση των ανόργανων σωματιδίων πολύ συχνά χρησιμοποιείται η μέθοδος ‘συλλογής ατμού’. Σύμφωνα με αυτή τη μέθοδο ατμός συμπυκνώνεται πάνω στα σωματίδια, τα μεγαλώνει σε ένα υπερκορεσμένο περιβάλλον και στη συνέχεια το υγρό δείγμα με το σωματίδια αναλύεται σε έναν ιοντικό χρωματογράφο. Ένα τέτοιο σύστημα είναι και ο δειγματολήπτης υγροποιημένων σωματιδίων (Steam-Jet Aerosol Collector, SJAC) [22]. Οι υπάρχουσες τεχνικές χρησιμοποιούνται για τη μέτρηση της σωματιδιακής φάσης. Παρακάτω θα περιγράψουμε ένα ημι-συνεχές σύστημα με το οποίο μπορεί να μετρηθεί και η αέρια και η σωματιδιακή φάση των ανόργανων ιοντικών συστατικών των σωματιδίων.

A7.1 ΑΠΟΤΕΛΕΣΜΑΤΑ-ΣΥΖΗΤΗΣΗ

Το σύστημα αυτό αποτελείται από 3 κυρίως μέρη:

(1) ένα σύστημα εναλλαγής μεταξύ μίας γραμμής με απογυμνωτές και μίας χωρίς απογυμνωτές. Οι απογυμνωτές είναι 2 σωλήνες με ομόκεντρους γυάλινους κυλίνδρους. Ο ένας επικαλύπτεται με όξινο διάλυμα για να συγκρατεί τα βασικά αέρια (NH_3) και ο δεύτερος με βασικό διάλυμα για τη συγκράτηση των όξινων αερίων (SO_2 , HNO_3 , HNO_2 , HCl). Η εναλλαγή μεταξύ αυτών των γραμμών γίνεται κάθε 30 min.

- (2) τον δειγματολήπτη υγροποιημένων σωματιδίων, ο οποίος είναι μια γυάλινη κατασκευή που αποτελείται από το χώρο ανάμιξης του ατμού με τα αεροζόλ όγκου 40 cm^3 και από 2 κυκλώνες από όπου συλλέγεται το υγρό δείγμα προς ανάλυση.
- (3) 2 χρωματογράφους για την ανάλυση των ανιόντων και κατιόντων σε πραγματικό χρόνο.

Με εναλλαγή μεταξύ της απογυμνωμένης και της μη απογυμνωμένης γραμμής μπορούμε να υπολογίσουμε τη σωματιδιακή και τη σωματιδιακή+αέρια φάση. Αφαιρώντας από τη σωματιδιακή+αέρια την σωματιδιακή φάση μπορούμε να υπολογίσουμε μόνο την αέρια. Εκτιμήσαμε αυτή τη τεχνική με μετρήσεις δειγματοληψίας ατμοσφαιρικών σωματιδίων $\text{PM}_{2.5}$ στο Ερευνητικό Ινστιτούτο Χημικής Μηχανικής (Ε.Ι.ΧΗ.Μ.Υ.Θ.) στη Πάτρα.

Για την αμμωνία (Εικόνα 9) και για το HONO το σύστημα έδωσε ικανοποιητικά αποτελέσματα. Καθώς η περιοχή είναι αγροτική η παρουσία της αμμωνίας είναι εντονότερη και επομένως πιο εύκολη η ανίχνευσή της. Συγκρίσεις με το θερμοδυναμικό μοντέλο ISORROPIA [23] έδειξαν πολύ καλή συμφωνία. Το νιτρικό οξύ ήταν σε μικρές συγκεντρώσεις κοντά στο όριο ανίχνευσης του συστήματος. Για το λόγο αυτό η εκτίμηση της τεχνικής αυτής θα πρέπει να γίνει σε κάποια αστική περιοχή, όπου υπάρχει αρκετό NO_x το οποίο θα οξειδωθεί προς νιτρικό οξύ.

Εικόνα 9: Αέρια NH₃ (γραμμή με τετράγωνα) από την διαφορά μεταξύ μετρήσεων με απογυμνωτές και χωρίς απογυμνωτές. Τα αποτελέσματα είναι σε καλή συμφωνία με τα προβλεπόμενα αποτέλεσμα από το θερμοδυναμικό μοντέλο ISORROPIA (καφέ διακεκομμένες γραμμές).

Α8 ΓΕΝΙΚΑ ΣΥΜΠΕΡΑΣΜΑΤΑ ΔΙΑΤΡΙΒΗΣ

Σε αυτή τη διδακτορική εργασία έγιναν γρήγορες μετρήσεις σύστασης και κατανομής των ατμοσφαιρικών σωματιδίων στο εργαστήριο και στο πεδίο και παράλληλα αναπτύχθηκαν μέθοδοι για τη βελτίωση της επεξεργασίας των δεδομένων. Συνδυάζοντας και μετατρέποντας διατάξεις συλλέχθηκαν πληροφορίες με τις οποίες εξηγούνται διαφορές μεταξύ μετρήσεων στο πεδίο και στο εργαστήριο.

Τα φάσματα μάζας του AMS αναλύθηκαν σε φάσματα μάζας χαμηλής, μέτριας και υψηλής πτητικότητας. Οι λιγότερο πτητικές ενώσεις ήταν και περισσότερο οξειδωμένες. Το φάσμα των λιγότερο πτητικών ενώσεων μοιάζει με αυτό που παρατηρείται στο πεδίο και αυτό σημαίνει ότι οι διαφορές στα φάσματα μεταξύ πεδίου και εργαστηρίου οφείλεται στη διαφορετική σύσταση πτητικότητας των οργανικών σωματιδίων.

Στη συνέχεια αναπτύχθηκε ένας αλγόριθμος ο οποίος υπολογίζει την πυκνότητα των οργανικών σωματιδίων και την CE του AMS. Ο αλγόριθμος αυτός εφαρμόστηκε

σε πειράματα δημιουργίας δευτερογενών οργανικών σωματιδίων σε περιβαλλοντικό θάλαμο και η μέση πυκνότητα των οργανικών σωματιδίων υπολογίστηκε στα $1.4 - 1.55 \text{ g cm}^{-3}$. Αυτή η σχετικά υψηλή τιμή σημαίνει ότι τα σωματίδια είναι στερεά (ή κερώδη). Επίσης οι προβλέψεις των τρισδιάστατων ατμοσφαιρικών μοντέλων μπορούν να διορθωθούν, καθώς αυτά χρησιμοποιούν μικρότερες τιμές πυκνότητας για τα οργανικά (π.χ. 1 g cm^{-3}).

Ο ίδιος αλγόριθμος εφαρμόστηκε και σε μετρήσεις πεδίου στην Φινοκαλιά της Κρήτης το καλοκαίρι του 2008 και τον χειμώνα του 2009 και υπολογίστηκαν η CE του AMS και η πυκνότητα των οργανικών. Η μέση CE για το καλοκαίρι βρέθηκε ίση με 0.85 ± 0.08 ενώ για τον χειμώνα 0.64 ± 0.13 . Η μέση πυκνότητα για το καλοκαίρι υπολογίστηκε στα $1.35 \pm 0.22 \text{ g cm}^{-3}$ και για τον χειμώνα στα $1.14 \pm 0.36 \text{ g cm}^{-3}$. Έτσι ο αλγόριθμος αυτός αφενός «διορθώνει» τα δεδομένα του AMS και αφετέρου δίνει πληροφορίες για τις φυσικές ιδιότητες των οργανικών σωματιδίων. Επιπλέον με τη μέθοδο αυτή μπορεί να υπολογιστεί η οργανική πυκνότητα και η CE των σωματιδίων που πέρασαν από τον θερμικό απογυμνωτή. Έτσι τα αποτελέσματα αυτά μπορούν να χρησιμοποιηθούν για να διορθωθεί η εκτιμώμενη πτητικότητα των οργανικών: στη περίπτωση του καλοκαιρινών μετρήσεων του 2008 τα οργανικά ήταν τουλάχιστον δύο τάξεις μεγέθους λιγότερο πτητικά από τα δευτερογενή οργανικά που παράγονται στο εργαστήριο.

Τέλος τροποποιώντας τη μέθοδο SJAC είναι δυνατή η μέτρηση της σωματιδιακής φάσης των ανόργανων ιοντικών ενώσεων (SO_4^{2-} , NO_3^- , NO_2^- , Cl^- , NH_4^+) αλλά και της αέριας φάσης (HNO_3 , HONO , NH_3) που βρίσκεται σε ισορροπία με τη σωματιδιακή. Το σύστημα ελέγχθηκε στο E.I.XH.M.Y.Θ και τα πρώτα

αποτελέσματα για την NH_3 και το HONO είναι ενθαρρυντικά. Ωστόσο για την ανίχνευση του HNO_3 απαιτείται ένα πιο αστικό περιβάλλον .

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Ph.D. Candidate in Chemical Engineering *2004 – Present*

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- Ph.D. Thesis title: “Usage of Aerosol Mass Spectrometry for the measurement of the physical and chemical properties of the atmospheric nanoparticles”.
- Research: Atmospheric particulate matter, physical and chemical properties of atmospheric organic aerosols, volatility of secondary organic aerosols, continuous measurements of organic and inorganic aerosols.
- Graduate Coursework: Thermodynamics, Applied Mathematics, Physical Chemistry, Inorganic Materials, Environmental Biotechnology, Renewable Energy, Separation Processes.

Dipl. Ing. in Chemical Engineering *1999-2004*

Department of Chemical Engineering, University of Patras, Greece

- Diploma Thesis: “Precipitation of struvite using an enzyme (alkaline phosphatase)”
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Graduate Research Assistant *2004 - Present*

University of Patras, Greece, Dept. of Chemical Engineering Air Quality Laboratory
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- Development of algorithms for the analysis of physical and chemical properties of the aerosols formed in the laboratory and at the field, development of new methods for semi-continuous measurements of inorganic particulate and gas phase.

- MEGAPOLI 2010 - winter field campaign. Field measurements using a TSI Scanning Mobility Particle Sizer (SMPS) and a thermodenuder.
- Finokalia Aerosol Measurement Experiment (FAME – 2009) field campaign. Field measurements using the Aerodyne's Aerosol Mass Spectrometer (AMS), a TSI Scanning Mobility Particle Sizer (SMPS) and a thermodenuder.
- Finokalia Aerosol Measurement Experiment (FAME – 2008) field campaign. Field measurements using the Aerodyne's Aerosol Mass Spectrometer (AMS), a TSI Scanning Mobility Particle Sizer (SMPS), a thermodenuder and a Steam Sampler.
- AEROMETRISI Field Campaign (January 2008) National Center of Scientific Research "Demokritos", Agia Paraskevi, Athens. Field measurements using our Steam Sampler.

Visiting Researcher

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Carnegie Mellon University, Center for Atmospheric Particle Studies, Pittsburgh PA

- Experiments in the Carnegie Mellon Smog Chamber investigating the formation and properties of biogenic secondary organic aerosol.

Instrumentation and programming skills

AMS, SMPS, Thermodenuder system, APS, Ion Chromatography, Steam Sampler, Atomic Absorption, FORTRAN, IGOR.

Undergraduate Research Assistant

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University of Patras, Greece, Dept. of Chemical Engineering Laboratory of Inorganic Chemistry

- Precipitation of struvite using an enzyme (alkaline phosphatase) using the techniques of Ion Chromatography and Atomic Absorption.

Research Assistant

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Liquid Fertilizers of Thrace (LI.FE.T), Komotini, Greece.

- Agricultural leaf and soil analysis using photometry UV, atomic absorption spectroscopy, distillation and other methods.

Graduate Teaching Assistant

Computer Programming for Chemical Engineers

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Thermodynamics II

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- Hildebrandt, L., Lee, B. H., Mohr, C., **Kostenidou, E.**, Tsimpidi, A. P., Karydis, V. A., Baltensperger, U., Donahue, N. M., Mihalopoulos, N., Pandis, S. N. and the FAME-08 AMS and Volatility Team, Characterizing the Composition and Volatility of Aged Organic Aerosol from Different Source Regions: The Finokalia Aerosol Measurement Experiment – 2008, European Geosciences Union (EGU) Meeting, 2009.
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- Kostenidou, E.**, Lee B. H., Engelhart, J. G., Pierce J. R., & Pandis S. N. Mass Spectra Deconvolution of Low, Medium and High Volatility Biogenic Secondary Organic Aerosol, European Aerosol Conference (EAC), 2008.
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HONORS AND AWARDS

2004 - 2006	Carnegie Mellon University Fellowship
2005	National Scholarship Foundation Award
2004	Technical Chamber of Greece Scholar Award
2003	National Scholarship Foundation Award
2003	Dimitrios K. Evangelou Award

SPOKEN LANGUAGES

Greek (native speaker)
English (fluent)
German (well)
Spanish (well)

PROFESSIONAL AFFILIATIONS

American Association for Aerosol Research (AAAR)
Hellenic Association for Aerosol Research (HAAR)
Technical Chamber of Greece