Sources and transformations of atmospheric aerosol particles

Author: Eben Spencer Cross

Persistent link: http://hdl.handle.net/2345/971

This work is posted on eScholarship@BC, Boston College University Libraries.

Boston College Electronic Thesis or Dissertation, 2008

Copyright is held by the author, with all rights reserved, unless otherwise noted.

Boston College

The Graduate School of Arts and Sciences

Department of Chemistry

SOURCES AND TRANSFORMATIONS OF ATMOSPHERIC

AEROSOL PARTICLES

A dissertation

by

EBEN SPENCER CROSS

Submitted in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

November 2008

© Copyright by EBEN S. CROSS

2008

SOURCES AND TRANSFORMATIONS OF ATMOSPHERIC AEROSOL PARTICLES

EBEN S. CROSS

Dissertation Advisor: PAUL DAVIDOVITS

ABSTRACT

Aerosol particles are an important component of the Earth-Atmosphere system because of their influence on the radiation budget both directly (through absorption and scattering) and indirectly (through cloud condensation nuclei (CCN) activity). The magnitude of the raditaive forcing attributed to the direct and indirect aerosol effects is highly uncertain, leading to large uncertainties in projections of global climate change. Real-time measurements of aerosol properties are a critical step toward constraining the uncertainties in current global climate modeling and understanding the influence that anthropogenic activities have on the climate.

The objective of the work presented in this thesis is to gain a more complete understanding of the atmospheric transformations of aerosol particles and how such transformations influence the direct and indirect radiative effects of the particles. The work focuses on real-time measurements of aerosol particles made with the Aerodyne Aerosol Mass Spectrometer (AMS) developed in collaboration with the Boston College research group. A key feature of the work described is the development of a light scattering module for the AMS. Here we present the first results obtained with the integrated light scattering – AMS system. The unique and powerful capabilities of this new instrument combination are demonstrated through laboratory experiments and field deployments.

Results from two field studies are presented: (1) The Northeast Air Quality Study (NEAQS), in the summer of 2004, conducted at Chebogue Point, Nova Scotia and (2) The Megacity Initiative: Local and Global Research Observations (MILAGRO) field campaign conducted in and around Mexico City, Mexico in March of 2006. Both field studies were designed to study the transformations that occur within pollution plumes as they are transported throughout the atmosphere. During the NEAOS campaign, the pollution plume from the Northeastern United States was intercepted as it was transported towards Europe. In this study, particles were highly processed prior to sampling, with residence times of a few days in the atmosphere. The MILAGRO campaign focused on the evolution of the Mexico City plume as it was transported north. During this study, regional and locally emitted particles were measured with residence times varying from minutes to days in the atmosphere. In both studies, the light scattering – AMS system provided detailed information about the density and composition of single particles, leading to important insights into how atmospheric processing transforms the particle properties. In Mexico City, the light scattering-AMS system was used for the first time as a true single particle mass spectrometer and revealed specific details about the atmospheric processing of primary particles from combustion sources.

To quantify the radiative effects of the particles on climate, the processing and ultimate fate of primary emissions (often containing black carbon or soot) must be understood. To provide a solid basis for the interpretation of the data obtained during the field studies, experiments were conducted with a well characterized soot generation-sampling system developed by the Boston College research group. The laboratory soot source was combined with the light scattering – AMS system and a Cloud Condensation Nuclei Counter (CCNC) to measure the change in cloud-forming activity of soot particles as they are processed in the atmosphere.

Because of the importance of black carbon in the atmosphere, several instruments have been developed to measure black carbon. In July of 2008, an intercomparison study of 18 instruments was conducted in the Boston College laboratory, with soot particles produced and processed to mimic a wide range of atmospherically-relevant conditions. Transformations in the physical, chemical, and optical properties of soot particles were monitored with the combined suite of aerosol instrumentation. Results from the intercomparison study not only calibrated the different instruments used in the study, but also provided critical details about how atmospheric processing influences the radiative effects of primary combustion particles.

ACKNOWLEDGEMENTS

Over the past five years I have had the privilege of working with some of the most enthusiastic, motivated and hard working individuals in the field of atmospheric chemistry. I have also been blessed with a network of supportive and loving friends and family. These colleagues, friends, and family have made it possible for me to complete the work described in this thesis.

First, I thank my advisor Professor Paul Davidovits for teaching me how to 'open my mind' to the different perspectives through which scientific problems can be approached. His kind and patient disposition have been much appreciated throughout the past five years. He has continually emphasized the importance of both science and life outside of science. I will carry the lessons learned from Paul through my life as a scientist and as a human being.

Among the outstanding people who have influenced my path in the world of science is Mr. Bob Raymond, my high school chemistry teacher. Mr. Raymond made it perfectly clear that if you work hard, you will get it, and if you are enthusiastic about what you are doing, working hard won't seem that bad. My enthusiasm for chemistry is a product of Mr. Raymond's enthusiasm and energy in front of the classroom.

I am especially grateful to Professor David Lewis who first introduced me, in the spring of 2003, to applied atmospheric chemistry and the Aerosol Mass Spectrometer with a 5:00 a.m. car ride from Connecticut College to Aerodyne Research. In addition to laying the groundwork for the light scattering project, Professor Lewis' generosity provided me with the opportunity to combine my interest for chemistry with my passion for the environment.

The members of the Boston College/Aerodyne research team have had a profound influence on my growth as a scientist over the past five years and I consider myself the luckiest graduate student on the planet to have been a part of this research team. I have had the privilege of working closely with Dr. Tim Onasch since my first day at Aerodyne. Tim's boundless excitement for, and knowledge of atmospheric chemistry has served as a constant source of motivation, energy and ideas throughout these last five years. Without Tim's help, I would not have made it. I thank Dr. Doug Worsnop for convincing me, at the beginning of this journey, that studying particles in the air was the most exciting and important subject that I could devote myself to as an environmental chemist. Since that time, particles have only become *more* exciting and *more* important. I thank Dr. John Jayne for his endless patience in teaching me how to repair the AMS after having broken it on numerous occasions and for being *the* outlier on the "niceness versus humanity" plot. I thank Dr. Jesse Kroll, Dr. Manjula Canagaratna, Dr. Leah Williams, and Dr. Achim Trimborn for sharing ideas, discussing different approaches to solving problems in the laboratory, and for always being friendly and encouraging. Finally, I thank Cameron Martin and all the members of the AMS User's community who continue to push aerosol science forward through collaborative efforts while maintaining a good sense of humor.

At Boston College, I was fortunate to work with a number of excellent young scientists including Dr. Jay Slowik, Dr. Silke Hings, Dr. Jeong-Ho Han, Erica Gagne,

Billy Wrobel and Adam Ahern each of whom contributed to the work presented in this thesis. A special thanks to Billy and Adam for their help in making the intercomparison study a great success and for helping me keep my sanity. I certainly would have lost it without the two of you. I also thank the Chemistry Department staff at Boston College especially, John Madden, Ginny Owens, Terri Wallace, Richard Pijar, and Kevin Sullivan for their help in all aspects of my work.

I would also like to thank my friends, Henry Kesner and Elisha Fielding for being great roommates and creating a friendly and cozy atmosphere to return to after long days in the lab. I was extremely lucky to have Cheryl and Michael Kraley as my second set of parents who opened their home to me for my first 15 months out in the 'real world' after graduating from college. I am indebted to late night conversations with Mac Cathles about all things Ph.D. and to Chad Dooley for his help coaching the Brookline Ligers and lending a hand with all things computational in the lab. A huge thankfulness goes to my lady, Meridith Greene who entered my life six months prior to my qualifying exam and is still here with me today. Her company brings me happiness each day. Special thanks goes to my parents, Peter and Candy, and sister, Emily who have always had confidence in my abilities and whose love and support have sustained me. Thank you.

In closing, I would like to share a quote from Paul, something that he told me during our first editing process together. "This [aerosol science] is much more difficult than giving birth to an elephant." Indeed...

This work was funded in part by the National Aeronautics and Space Administration through the Earth System Science Fellowship Program; by

iii

the Atmospheric Chemistry Program of the National Science Foundation (NSF) grant No. ATM-0525355, and by the Office of Biological and Environmental Research of the Department of Energy (Atmospheric Science Program) grant Nos. DE-FG02-05ER63995 DE-FG02-05ER84268, and DOE DE-FG02-05ER63982.

•

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
TABLE OF CONTENTS	v
LIST OF FIGURES	X
LIST OF TABLES	xvi
CHAPTER I. INTRODUCTION	1
1.1 BACKGROUND	2
1.2 THE ENERGY BUDGET	
1.3 RADIATIVE FORCING	7
1.4 ATMOSPHERIC AEROSOL PARTICLES	12
1.4.1 General Considerations	13
1.4.2 Sources of Aerosol Particles	13
1.4.3 Aerosol Particle Atmospheric Lifetime	14
1.4.4 The Size of Atmospheric Aerosol Particles	15
1.4.5 The Challenge of Measuring Atmospheric Aerosol Particles	17
1.5 SUMMARY OF THE CURRENT WORK	18
1.6 SYMBOLS AND ABBREVIATIONS	22
1.7 LIST OF PUBLICATIONS	22
1.8 REFERENCES FOR CHAPTER I	23
CHAPTER II. INSTRUMENTAL METHODS	26
2.1 OVERVIEW	27
2.2 INSTRUMENT DESCRIPTIONS	28
2.2.1 Combined Optical and Vacuum Aerodynamic Diameter Measurements	29
2.2.1.1 Aerodyne Aerosol Mass Spectrometer (AMS)	30
2.2.1.2 Light Scattering Module	34
2.2.2 Differential Mobility Analyzer (DMA)	36
2.2.3 Condensation Particle Counters (CPC)	37
2.2.4 Scanning Mobility Particle Sizer (SMPS)	37
2.2.5 Combined CCN and SMPS-AMS Measurements	38
2.2.5.1 Cloud Condensation Nuclei Counter (CCNC)	38
2.3 LABORATORY SOOT SOURCE	41
2.4 REFERENCES FOR CHAPTER II	41

CHAPTER III. PARTICLE DENSITY MEASUREMENTS USING A LIGHT SCATTERING MODULE COUPLED TO AN AEROSOL MASS SPECTROMETER

	45
3 1 OVERVIEW	46
3 2 BACKGROUND SUMMARY OF PARTICLE DENSITY MEASUREMENTS	47
3.2.1 Instruments used for measuring the density narameters	49
3.2.2 Ontical Sizing Measurements	51
3.2.3 Real-Time Density Determination with a LS-AMS	52
3 3 THEORETICAL BASIS FOR THE LS-AMS DENSITY DETERMINATION	54
3 4 FXPERIMENTAL	57
3.4.1 Production of Characterized Aerosol Particles	57
3 4 2 Instrumentation	58
3 4 2 1 AMS Apparatus	58
3 4 2 2 Light Scattering Module	59
3 4 3 LS-AMS as a Potential Collection Efficiency Diagnostic	60
3 4 4 Time-of-flight Measurement	61
3 5 UNCERTAINTY IN THE LS-AMS DENSITY MEASUREMENT	61
3.5.1 Accuracy of time-of-flight determination	62
3.5.1.1 Determination of t ₀	62
3512 Determination of t_f	62
$3.5.2$ Overall Uncertainty in Particle Time-of-Flight and d_{y_2}	. 64
3.5.3 Uncertainty in Particle Size Determination Using Scattered Light Intensity	65
3.5.4 Uncertainties Due to Assumptions	66
3.5.4.1 Non-spherical particles	67
3.5.4.2 Absorbing Aerosol Particles	67
3.6 LABORATORY CHARACTERIZATION - RESULTS AND DISCUSSION	68
3.6.1 Single particle scattered light pulse	68
3.6.2 Measurement of Vacuum Aerodynamic Diameter (d _{va})	69
3.6.3 Measurement of Scattered Light Intensity (R _{LS})	70
3.6.4 Correlation Between R_{IS} and d_n	73
3.6.5 Determination of Particle Density	79
3.6.6 Density Resolution of the LS-AMS Instrument	82
3.7 AMBIENT AEROSOL ENSEMBLE DENSITY MEASUREMENTS	84
3.7.1 Field Study Background	84
3.7.2 Ambient Aerosol Particle Density Determination	85
3.7.3 Mixing State of the Ambient Aerosol Particles	90
3.7.4 Consistency Check of ots via Average Single Particle Composition	92
3.8 SUMMARY	. 93
Appendix 3A. Effect of Laser and Particle Beam Profiles on LS-AMS Optical	
Response	94
1	

Appendix 3B. Comparison of the Experimental Response of LS-AMS to Mie The	ory
	96
3.9 REFERENCES FOR CHAPTER III	97

4.1 OVERVIEW	103
4.2 INTRODUCTION	. 104
4.2.1 Brief Survey of Single Particle Mass Spectrometry	. 109
4.3 EXPERIMENTAL METHODS	113
4.3.1 Instrumentation	113
4.3.1.1 LS-ToF-AMS	113
4.3.2 Data Acquisition	. 115
4.3.2.1 Mass Spectrum (MS) and Particle Time of Flight (PTOF) Modes	. 115
4.3.2.2 Brute Force Single Particle (BFSP) Mode	. 117
4.3.2.3 Light Scattering Single Particle Mode (LSSP)	117
4.4 SINGLE PARTICLE ANALYSIS	120
4.4.1 Single Particle Collection and Detection	120
4.4.1.1 Uncertainty in Single Particle Mass Measurements	126
4.4.2 Single Particle Chemical Composition	128
4.4.3 Comparison of Single Particle and Ensemble Measurements	132
4.4.4 Mixing State Determination	135
4.5 RESULTS AND DISCUSSION	139
4.5.1 Sampling Site and Meteorology	139
4.5.2 Aerosol Ensemble Properties	. 140
4.5.3 Single Particle Chemical Compositions	. 144
4.5.3.1 Biomass Burning Organic Aerosol (BBOA) Particles	. 145
4.5.3.2 Inorganics	. 147
4.5.4 Mixing State of the Ambient Aerosol	148
4.5.4.1 Primary HOA particles and their processing	153
4.5.4.2 Influence of atmospheric processing on particle composition	158
4.5.4.3 SO ₂ plume event	162
4.5.4.4 High chloride content single particles	163
4.6 SUMMARY	167
4.7 REFERENCES FOR CHAPTER IV	169

CHAPTER V. CCN ACTIVATION EXPERIMENTS 180 5.1 OVERVIEW 181 5.2 BACKGROUND AND THEORY 182 5.2.1 Influence of Surface Tension on S_c 184

5.2.2 Mapping S _c as a Function of Particle Size and Composition	185
5.2.3 Role of Particle Phase in Activation of Single-Component Aerosols	187
5.2.4 Determination of the Particle Shape Factor	190
5.2.5 Considerations for CCN Activity of Coated Ammonium Sulfate Particles	191
5.3 EXPERIMENTAL	192
5.3.1 Apparatus	192
5.3.2 Cloud Condensation Nuclei Counter	193
5.3.3 Measurement of S _c	194
5.3.4 Combining Measurements of CCN activity with SMPS and AMS	
Measurements	196
5.3.5 Summary of Particle Generation Techniques	197
5.3.5.1 Ammonium Sulfate Particles	197
5.3.5.2 Adipic Acid Particles	197
5.3.5.3 Soot Particles	198
5.4 RESULTS AND DISCUSSION	199
5.4.1 Experiments with Ammonium Sulfate	199
5.4.1.1 Adipic acid-coated ammonium sulfate particles	201
5.4.1.2 Oleic acid-coated and DOS-coated ammonium sulfate	202
5.4.1.3 Stearic-acid coated ammonium sulfate	204
5.4.1.4 Conclusions for CCN activation experiments with coated ammonium	
sulfate	205
5.4.2 Experiments with Adipic Acid	206
5.4.2.1 Previously published S _c data for adipic acid	207
5.4.2.2 Dry Adipic Acid Particles Generated by Atomization	209
_Toc2134208765.4.2.3 Homogenously Nucleated Dry Adipic Acid Particles	209
5.4.2.4 Comparison with Previous Studies	212
5.4.2.5 Wet Adipic Acid	214
5.4.2.6 Conclusions of CCN activity experiments with adipic acid	215
5.4.3 Soot Particle CCN Studies	216
5.4.3.1 Nascent uncoated soot	217
5.4.3.2 Soot Coated with Adipic Acid	218
5.4.3.3 Soot Particles Coated with Sulfuric Acid (H ₂ SO ₄)	220
5.4.3.4 CCN Activity of Oxidized Soot Particles with the Potential Aerosol M	A ass
(PAM) Instrument	222
5.4.3.5 Conclusions to CCN activation studies of soot particles	224
5.5 SUMMARY	225
5.6 APPENDIX 5A: CCN Instrument Calibration	226
5.7 REFERENCES FOR CHAPTER V	229

CHAPTER VI. INTERCOMPARISON STUDY OF BLACK CARBON	
INSTRUMENTS JULY 2008	234
6.1 OVERVIEW	
6.2 LESSONS LEARNED FROM 1 st INTERCOMPARISON STUDY	

6.3 PREPARATION FOR 2 ND INTERCOMPARISON STUDY (BC ²)	237
6.4 SUMMARY OF 2 ND INTERCOMPARISON STUDY (BC ²)	240
6.4.1. Instruments Studied during the 2 nd Intercomparison	241
6.4.2. Experimental Objectives and Highlights	244
6.4.3. Highlights from BC^2	247
6.5 REFERENCES	248

LIST OF FIGURES

Figure 1-1. Estimate of the global mean energy balance.

Figure 1-2. Magnitude and uncertainty in the radiative forcing attributed to the different components of the Earth-atmosphere system.

Figure 2-1. Schematic of the Q-AMS.

Figure 2-2. Schematic of the LS-ToF-AMS.

Figure 2-3. Components and Orientation of Light Scattering Module.

Figure 2-4. Schematic of the DMT CCNC instrument (Roberts and Nenes, 2005).

Figure 2-5. Soot Source and Sampling Configuration.

Figure 3-1. Laboratory apparatus for aerosol generation and characterization.

Figure 3-2. Percent difference in the particle d_{va} as a function of d_{va} for two different time-of-flight determinations.

Figure 3-3. Scattered light pulse for an oleic acid particle of $d_m = 322$ nm.

Figure 3-4. Measured number distributions as a function of particle d_{va} for a monodisperse distribution of oleic acid particles at $d_m = 322 \text{ nm} + -30 \text{ nm}$. The dashed line is the distribution with t_0 determined with a 2% chopper slit width. The solid line is the distribution with t_0 determined with the scattered light pulse.

Figure 3-5. Experimental response of the LS-AMS for oleic acid monodisperse size distribution $d_m = 322$ nm compared with the calculated response using Mie theory.

Figure 3-6. Scattered light intensity for oil particles with refractive index n = 1.53 as a function of particle physical diameter. The solid line is a calculation based on Mie theory.

Figure 3-7. Scattered light intensity for oil particles with refractive index n = 1.53 as a function of particle physical diameter for both monodisperse (solid circles) and polydisperse (open circles) distributions. The solid line is a calculation based on Mie theory.

Figure 3-8. Scattered light intensity for oil particles for index of refraction between 1.30 < n < 1.66. The dashed lines are calculations based on Mie theory. The chosen calibration curve is shown as the solid black line.

Figure 3-9. Single particle density distribution (ρ_{LS}) for refractive index oil n = 1.47. Density obtained from the mode of a Gaussian fit to these points is 0.87 ± 0.11 g/cm³.

Figure 3-10. Single particle densities (ρ_{LS}) versus material density (ρ_m) for all spherical particles studied. Particles across a refractive index range 1.33 – 1.66 were tested.

Figure 3-11. Scattered light intensity (R_{LS}) distributions (Upper Panel) and corresponding ρ_{LS} distributions (Lower Panel) for four known composition aerosol particles.

Figure 3-12. Lower panel: Average mass concentrations of the major chemical species measured with the LS-AMS at Chebogue Point, Nova Scotia. Upper Panel: Densities determined from average chemical composition (ρ_{cc}) (shown as the black line) and densities determined from the average single particle optical scattering (ρ_{LS}) (shown as the grey line).

Figure 3-13. Correlation between the average values of ρ_{cc} and ρ_{LS} measured for the 5 week period of ambient aerosol particle sampling at Chebogue Point.

Figure 3-14. Single particle density distributions for sulfate-dominated (event A shown as the solid line) and organic-dominated (event B shown as the dashed line) ambient aerosol measured with the LS-AMS at Chebogue Point, Nova Scotia.

Figure 3A-1. Two laser beam intensity profiles measured by translating a 350 nm beam of NH_4NO_3 particles across the vertical (Y) axis of the laser and measuring the scattering signal as a function of particle position. The shaded distribution illustrates the calculated width of a 350 nm NH_4NO_3 particle beam based on results from the beam width probe.

Figure 4-1. Total particle counts (in grey) and number fractions of prompt (blue), delayed (green) and null (black) particles as a function of time-of-flight (i.e. d_{va}).

Figure 4-2. Measured single particle mass obtained from chemical ion signals plotted versus single particle mass obtained from optical diameter (d_o) and vacuum aerodynamic diameter (d_{va}) measurements for (a) particles with prompt vaporization and (b) particles with delayed vaporization.

Figure 4-3. Average HOA and OOA organic mass spectra obtained from ambient ensemble measurements using PMF analysis (upper region, plots a and c) and two-component PCA analysis (lower region plots b and d).

Figure 4-4. Six single particle mass spectra obtained for three different sized organic particles ($d_o \sim 200$, 250, and 350 nm) predominately composed of HOA (a-c) and OOA (d-f) components. Particle d_{va} , d_o , and mass are shown in the insert.

Figure 4-5. (a) Average mass distributions as a function of particle time-of-flight for ensemble data (dashed black line) and total single particle data (red line). Distributions for prompt (blue), delayed (green) and null (black) particles are also shown. (b) Correlation plot between the average PToF and total single particle mass measurements for times-of-flight between 3.1-5.5 ms, denoted with arrows in (a).

Figure 4-6. Light scattering signals (upper panel) and chemical ion signals (middle panel) as a function of particle time-of-flight for a single chopper cycle in which two particles entered the LS-ToF-AMS. The lower panel displays the mass spectrum of each particle.

Figure 4-7. Average ensemble mass concentrations (measured in MS mode) as a function of sampling time. (a) Organic components obtained from PMF analysis – OOA, BBOA, and HOA. (b) Chemical components obtained from traditional AMS fragmentation patterns – organic, nitrate, sulfate, ammonium, and chloride. Average diurnal cycles, for the full 75 hour sampling period, of each chemical component are displayed in plots (c) and (d).

Figure 4-8. Average ensemble mass distributions (measured in PTOF mode) as a function of vacuum aerodynamic diameter (d_{va}) for (a) HOA and OOA components and (b) organic, nitrate, sulfate, ammonium, and chloride.

Figure 4-9. Time series of NH_4Cl , $(NH_4)_2SO_4$, NH_4NO_3 , OOA, and HOA single particle mass fractions. Data points are colored by HOA mass fraction as indicated in the upper left.

Figure 4-10. Particle counts (lower panel) and average single particle composition (upper panel) as a function of HOA mass fraction.

Figure 4-11. Time trends in the (a) measured number and (b) number fraction of high-HOA, intermediate-HOA, and low-to-zero-HOA particles.

Figure 4-12. Time trends in the number (upper panel) and number fraction of 'coated' particles for (a) intermediate-HOA particles and (b) low-to-zero-HOA particles.

Figure 4-13. (a) Measured (i.e. real) single particle NH_4 mass plotted versus calculated single particle NH_4 mass for the subset of single particles with high chloride content. (b) Single particle mass spectrum for a typical high chloride content particle (identified in (a) with the arrow).

Figure 5-1. Calculated supersaturation S as a function of the solution droplet diameter d_p for a particle composed of adipic acid. The adipic acid particle has a dry diameter of 145 nm and a critical supersaturation S_c of 0.166%.

Figure 5-2. Critical supersaturations as a function of initially dry particle diameter, calculated from Köhler theory for ammonium sulfate (red), adipic acid (yellow) and an insoluble but wettable substance (black). The lines for adipic acid have been modeled in two different ways: using the surface tension of water (dashed line) and using a concentration-dependent surface tension defined by the Szyszkowski-Langmuir equation (solid line). See text for details.

Figure 5-3. Calculated deliquescent supersaturations S_{del} (plotted on the S_c axis) as a function of the dry particle diameter for adipic acid using water activities of 0.990 (gray) and 0.997 (green). The upper bound for each activity corresponds to a surface tension of 0.072 J/m² while the lower bound corresponds to a surface tension of 0.060 J/m².

Figure 5-4. Schematic of experimental apparatus used during the CCN experiments.

Figure 5-5. Sample activation curves for 31 nm (red) and 45 nm (blue) ammonium sulfate particles. The critical supersaturation (S_c) calculated from the critical temperature (dT_c) is the supersaturation where 50% of the particles are activated.

Figure 5-6. S_c plotted as a function of particle diameter for adipic acid coated ammonium sulfate particles of sizes $d_{core} = 34$ nm (black), 53 nm (green) and 73 nm (blue) The dashed lines are calculated using Köhler theory.

Figure 5.7. S_c plotted as a function of particle diameter for oleic acid (pink diamonds) and DOS (green circles) coated ammonium sulfate particles. The dashed lines are calculated using modified Köhler theory using a water solubility of 0.1 kg/mL for each of the coating materials.

Figure 5-8. S_c plotted as a function of particle diameter for stearic acid-coated ammonium sulfate particles of sizes $d_{core} = 37$ nm, 55 nm and 76 nm.

Figure 5-9. Published critical supersaturations (S_c) for adipic acid as a function of dry particle size. Particles were obtained by atomizing aqueous solutions. The source of the data is shown by the symbols as identified in the insert. The state of the particles prior to

activation was dry unless otherwise noted. Critical supersaturations predicted by the standard Köhler theory are shown as solid lines for ammonium sulfate (red line), adipic acid (orange line), and an insoluble but wettable substance (black line). See text for details.

Figure 5-10. *S_c* plotted as a function of particle diameter for dry adipic acid particles (blue symbols). Köhler theory lines are the same as in Figures 5-1 and 5-3. The shaded area is the deliquescence region calculated from Eq. 5-4 with $\gamma_w = 0.990$. The upper and lower bounds correspond to solution surface tensions of 0.072 and 0.060 J/m², respectively.

Figure 5-11. S_c plotted as a function of particle diameter for dry adipic acid particles from previously published studies (as in Figure 5-1) shown together with our measurements.

Figure 5-12. Plot of S_c as a function of wet adipic acid particle diameter. Data from present work are displayed as blue points. Data of Bilde and Svenningsson (2004) are shown as light blue stars.

Figure 5-13. S_c plotted as a function of the total particle diameter (soot core + adipic acid coating) for adipic acid coated soot particles of sizes $d_{core} = 88$ nm (diamonds), 102 nm (squares), 136 nm (triangles), and 181 nm (circles). Also included are the results for dry adipic acid obtained in this study (blue).

Figure 5-14. S_c plotted versus coated particle diameter for three different size soot cores coated with H₂SO₄ (See text for details).

Figure 5-15. CCN activation curves (CCN/CPC) as a function of supersaturation for 163 nm soot particles exposed to increasing concentrations of OH and O₃ within the Potential Aerosol Mass (PAM) instrument.

Figure 5A-1. Calculated critical supersaturation as a function of CCN instrument dT. The instrument flow rate was 0.93 L/min.

Figure 5A-2. Calculated critical supersaturation as a function of CCN instrument dT. The instrument flow rate was 1 L/min.

Figure 6-1. Soot generation-sampling apparatus used during the 1st intercomparison study.

Figure 6-2. Improved soot generation-sampling system apparatus with alignment controls. Stainless steel support structure not shown.

Figure 6-3. Range of wavelengths covered with optical measurements used during the BC^2 study. The direct circumsolar radiance in W/m^2 is plotted as a function of wavelength in the lower panel.

Figure 6-4. Schematic of the sampling configuration during the BC^2 intercomparison study.

LIST OF TABLES

Table 3-1. Composition, refractive index, and material density for all spherical particles studied with the LS-AMS.

Table 5-1: Estimated particle dynamic shape factors as a function of particle size for dry adipic acid generated by homogeneous nucleation.

Table 6-1. Highlights from the BC^2 intercomparison study

Table 6-2. List of scientists and their institutional affiliations that participated in the BC^2 study.

CHAPTER I

INTRODUCTION

1.1 BACKGROUND

The field of atmospheric chemistry has recently gained the attention of the general public because of issues associated with climate change. Projections of catastrophic events including sea level rise and increasingly violent storms in connection with manmade climate change have reached a fearful and captivated audience of economists, policy makers, media outlets, and the general public. The underlying science of climate change relies on a multi-disciplinary combination of historical data, global climate modeling and real-time atmospheric measurements and observations. The 2007 Nobel peace prize was awarded jointly to Al Gore (for his documentary on climate change) and the scientists on the Inter-Governmental Panel on Climate Change (IPCC) who established a comprehensive, cross-disciplinary overview of the current scientific knowledge about climate change (IPCC Fourth Assessment Report, 2007). Such recognition emphasizes the central importance of climate change in the lives and future of all who inhabit planet Earth. Although the overwhelming majority of the scientific community accepts global warming as a well documented phenomenon, the rate of warming and the role of anthropogenic factors in the warming process are still not well understood. At present, the effects of atmospheric aerosol particles present the largest uncertainties in the quantification and modeling of global climate change.

The objective of the work described in this thesis is to improve our understanding of the physical and chemical properties of atmospheric aerosol particles. The work includes instrument development, laboratory experiments, and ambient aerosol sampling. In this chapter, we outline the basic principles of the Earth's energy budget and identify the components within the Earth-atmosphere system that influence radiation. This is followed by an overview of the properties of atmospheric aerosol particles and the challenges one must face when devising aerosol measurement strategies. The chapter closes with a summary of the work presented in the subsequent chapters of the thesis.

1.2 THE ENERGY BUDGET

The Earth's primary source of energy is the sun (> 99%). To visualize how radiation interacts with the Earth-atmosphere system, consider a view of Earth from space: clouds and snow-covered regions appear white, continental regions appear in varying degrees of green and brown, and the oceans are blue. This image of Earth is the consequence of varying degrees of reflection and absorption by the components of the Earth-atmosphere system. The bright white clouds and snow-covered peaks reflect more sunlight than the oceans and continents. This is due to the higher reflectance, or albedo, of clouds and ice compared to the reflectance of soil or liquid water. The global mean planetary albedo (R_p) defines the fraction of incoming solar radiation reflected back into space by clouds, air molecules, atmospheric particles, and the Earth's surface. Approximately 30% of the total incoming solar radiation is reflected back into space with approximately 2/3 reflected by clouds and 1/3 reflected by atmospheric constituents (primarily aerosol particles) and Earth's surface (Seinfeld and Pandis, 2006). Of the remaining incoming solar radiation, approximately 50% is absorbed by the Earth's surface and 20% is absorbed by atmospheric constituents. In return, the Earth's surface emits energy back into the atmosphere via thermal infrared radiation, latent heat contained in evaporated water vapor, or sensible heat (local heating of the air in contact with the Earth's surface). The majority of this emitted energy is in the form of longwave infrared radiation. Compared to incoming shortwave UV/Visible solar radiation, longwave radiation is preferentially absorbed by gas phase species in the atmosphere. After absorption by these species, radiation is re-emitted in all directions with a portion eventually released from the Earth-atmosphere system to space.

To understand the energy balance of the Earth-atmosphere system, it is necessary to quantify the flux density of incoming and outgoing energy at the top of Earth's atmosphere. This balance of energy is summarized in equation 1-1 as:

$$F_{net} = F_{s,i} - (F_{s,r} + F_l) \tag{1-1}$$

The terms $F_{s,i}$, $F_{s,r}$, and F_l are the flux densities of incoming solar radiation, reflected solar radiation, and emitted longwave radiation respectively. The equation shows that for energy balance (*i.e.* $F_{net} = 0$) to occur, the sum of emitted longwave radiation and reflected solar radiation must equal the total incoming solar radiation measured at the top of the atmosphere. This balance is shown schematically in Figure 1-1. At the top of the atmosphere, $F_{s,i} = 342 \text{ W/m}^2$, $F_{s,r} = 107 \text{ W/m}^2$, and $F_l = 235 \text{ W/m}^2$. Under these conditions, the temperature of the Earth remains constant. Changes to the earth-atmosphere system (such as an increase in greenhouse gas concentration or the number concentration of aerosol particles) result in $F_{net} \neq 0$. The temperature of the Earth will either decrease ($F_{net} < 0$) or increase ($F_{net} > 0$) in response to the change.

Figure 1-1 also summarizes the emission-absorption processes that occur within the Earth-atmosphere system. At the surface of the Earth, the flux density of emitted infrared radiation is a function of the temperature of the surface. On average the Earth's surface is 15°C which corresponds to a total emissive flux of 390 W/m². The total emissive flux of the Earth is calculated via Equation 1-2, which relates the radiation emitted by a blackbody to its absolute temperature:

$$F = \sigma T^4 \tag{1-2}$$

Here, *F* is the radiation emitted by a blackbody (i.e. the earth), σ is the Stefan-Boltzmann constant (5.671x10⁻⁸ W m⁻² K⁻⁴), and *T* is the temperature of the blackbody. The spectral irradiance of the sun (another example of a blackbody) peaks in the visible region of the electromagnetic spectrum with ~40% of all incoming solar radiation within the wavelength range of 0.4 - 0.7 µm (*Seinfield and Pandis*, 2006). Incoming radiation is not effectively absorbed by atmospheric gases at these wavelengths. The atmosphere is nearly opaque to radiation with $\lambda < 290$ nm. The absorption here is mostly due to O₂ and O₃ molecules. On the other hand, the radiation emitted from the Earth's surface is mostly 10 < $\lambda < 25$ µm. Within this range, the gas molecules CO₂ and H₂O are strongly absorbing. As a result, the net effect of atmospheric species such as water vapor and greenhouse gases is to decrease the flux of longwave radiation reaching the top of the atmosphere, warming the planet.



Figure 1-1. Estimate of the global mean energy balance. (*Kiehl and Trenberth*, 1997)

Three types of changes to the Earth-atmosphere system will alter the radiative balance and thus the temperature of the Earth: (1) A change in the incoming solar radiation ($F_{s,i}$) (e.g. by variations in the solar irradiance), (2) a change in the reflectivity of the Earth-atmosphere system ($F_{s,r}$) (e.g. by changes in particles, cloud cover, or land-use), or (3) a change in the amount of infrared radiation that is released to space (F_i) (e.g. an increase in atmospheric concentration of greenhouse gases or water vapor). Perturbations in the radiative balance are expressed as radiative forcings, in W/m². In 2007, the IPCC calculated the radiative forcing due to each of the major factors of the Earth-atmosphere system that influence climate (*IPCC*, 2007). These results will be summarized in the following section.

1.3 RADIATIVE FORCING

The technical definition of radiative forcing used by the IPCC is: 'the change in net (down minus up) irradiance (solar plus longwave; in W/m^2) at the tropopause¹ after allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at unperturbed values' (*Ramaswamy et al.*, 2001). This rather complex definition is to be understood in the following way. The natural response of the earth-atmosphere system to an energy imbalance is to either cool or warm. The energy imbalance (radiative forcing) at the top of the atmosphere is determined by holding the Earth surface and troposphere temperature constant.

Radiative forcing (RF) values are reported as the difference in RF between current (~2005) and pre-Industrial revolution (1750) atmospheric conditions. Therefore, depending on how a given factor (e.g. greenhouse gas, aerosol particle, land use) has changed since the Industrial revolution, it can have either a positive (warming) or a negative (cooling) radiative forcing effect on the climate. In addition to estimating the sign and magnitude of each component's RF value, the uncertainty (statistical value) and current level of scientific understanding (structural uncertainty) of each component is provided.

The total radiative forcing due to all components of the Earth-atmosphere system originating from anthropogenic activities is estimated to be +1.6 [-1.0,+0.8] W/m² (*IPCC*,

¹ The tropopause is located between the troposphere and stratosphere and is typically found at an altitude of \sim 15 km.

2007). The numbers in the brackets are the 90% confidence interval (minus sign determining the lower limit (A-X), plus sign determining upper limit in the form (A+Y).

In addition to carbon dioxide (CO₂), the long-lived anthropogenic greenhouse gases are methane (CH₄), nitrous oxide (N₂O), halocarbons(CFC's) and sulfur hexafluoride (SF₆). The current RF due to greenhouse gases is +2.63 [±0.26] W/m² (*IPCC* 2007; and *Collins et al.*, 2006). In addition to greenhouse gases, the IPCC identifies six other components within the Earth-atmosphere system that influence climate. These are ozone (including tropospheric and stratospheric), water vapor produced by oxidation of stratospheric CH₄, surface albedo (R_p), total aerosol, linear contrails, and solar irradiance. With the exception of solar irradiance, changes in these parameters since the Industrial revolution are considered anthropogenic. The radiative forcing, spatial scale, and level of scientific understanding (LOSU) of each component are listed in Figure 1-2.

Although water vapor is the most abundant greenhouse gas in the atmosphere, it is not included in the list of radiative forcing agents in Figure 1-2 because human activities do not have a strong *direct* influence on water vapor concentrations. However, the water vapor concentration in the atmosphere is indirectly influenced by human activities. For example, as the climate warms (largely due to anthropogenic activities), more water vapor is released into the atmosphere, which subsequently absorbs more infrared radiation causing further warming. This process is considered a positive feedback because the response of the system amplifies the initiating change.



RADIATIVE FORCING COMPONENTS

Figure 1-2. Magnitude and uncertainty in the radiative forcing attributed to the different components of the Earth-atmosphere system (*IPCC*, 2007).

Anthropogenic aerosol is the second strongest radiative forcing agent of the Earth-atmosphere system. The cumulative effect of aerosols is to cool the climate, offsetting the warming influence of the long-lived greenhouse gases to some extent. One key difference between aerosols and greenhouse gases is that aerosol particles remain in the atmosphere for only a few weeks whereas greenhouse gases last for hundreds of years in the atmosphere. As a result, the spatial distribution of aerosol particles is highly

dependent on the strength and number of particle sources within a given area. Notice that the uncertainty in the RF of aerosols is much larger than that of the greenhouse gases and the level of scientific understanding is listed as 'low' indicating that the radiative properties of aerosols are not well characterized. The non-uniform distribution of aerosol particles in the atmosphere is one reason for this large uncertainty.

Aerosol particles influence the radiation budget directly and indirectly and these effects are differentiated in Figure 1-2 as the direct effect and cloud albedo effect respectively. The direct effect is due to the scattering and/or absorption of incoming solar radiation by the particles. The extent to which a given aerosol particle will scatter or absorb light depends on the chemical composition, size, morphology, and atmospheric residence time of the particle. Most atmospheric particles tend to scatter rather than absorb incoming solar radiation. Atmospheric salt species (*e.g.* ammonium sulfate, ammonium nitrate, and sodium chloride) are examples of particles that exclusively scatter incoming solar radiation. These types of particles increase the reflectivity of the Earth-atmosphere system and decreasing the total energy flux reaching the Earth's surface. Therefore, particulate salt species have a net a negative radiative forcing influence.

In contrast to particulate salt species, soot particles originating from biomass burning or combustion sources can absorb as well as scatter incoming radiation. Soot particles, containing black carbon, are one of the key atmospheric species capable of absorbing incoming solar radiation. With increased atmospheric residence time, soot particles are often coated with atmospheric salt species and/or oxidized organics. Such coatings can enhance the absorption of the original soot particle by focusing more light into the soot core. Soot particles have a net positive radiative forcing influence, resulting in a warmer climate.

Current measurements and models show that ambient aerosols scatter more incoming solar radiation than they absorb. Such enhanced scattering increases the planetary albedo (or reflectivity) causing a decrease in the amount of solar radiation absorbed by the Earth and atmosphere. The net result of aerosol particles is therefore to cool the planet. On average, the radiative forcing attributed to the total aerosol direct effect is -0.5 [\pm 0.4] W/m² (See Figure 1-2).

The IPCC report estimates the direct effect of the various types of aerosol particle mass as follows: sulfate, -0.4 [\pm 0.2] W/m²; fossil fuel organic carbon, -0.05 [\pm 0.05] W/m²; fossil fuel black carbon, +0.2 [\pm 0.15] W/m²; biomass burning, +0.03 [\pm 0.12] W/m²; nitrate, -0.1 [\pm 0.1] W/m²; and mineral dust, -0.1 [\pm 0.2] W/m². The uncertainty in the RF values for individual aerosol species is high due to limited real-time measurements of aerosol concentration, size, and shape throughout the troposphere. As stated earlier, black carbon and biomass burning aerosol particles have net positive (warming) RF values while the other aerosol species have net negative (cooling) RF values.

The formation of cloud droplets in the atmosphere requires a nucleus which is provided by atmospheric aerosol particles. These cloud-droplet-forming particles are called cloud condensation nuclei (CCN). The indirect or cloud albedo effect refers to the process of particles acting as CCN. The cloud then influences the radiative budget by scattering and absorbing incoming solar radiation and absorbing surface-emitted infrared radiation. The radiative influence of a given cloud depends on its altitude, location, and microphysical properties. Clouds formed in polluted atmospheres with high number concentrations of aerosol particles tend to consist of a higher number of smaller water droplets. This microphysical structure decreases the precipitation efficiency of the cloud and increases the cloud's atmospheric lifetime and reflectivity. The overall influence of the aerosol indirect effect is to cool the planet. The current RF due to the aerosol indirect effect is -0.7 [-1.1, +0.4] W/m² as shown in Figure 1-2. Note that the uncertainty in the aerosol indirect effect is larger than any of the other individual uncertainties. Without improvements in the measurement and characterization of atmospheric aerosols as cloud condensation nuclei, the current evaluation and future projections of man-made climate change will remain uncertain.

1.4 ATMOSPHERIC AEROSOL PARTICLES

An aerosol is defined as a suspension of fine liquid or solid particles in a gas (*Hinds*, 1999). Atmospheric aerosol particles include dust, mist, fog, haze, fume, smoke, and smog (*Seinfeld and Pandis*, 2006). Cloud droplets are not considered to be aerosol particles.

1.4.1 General Considerations

Although the main focus of this work is the atmospheric/radiative aspect of aerosols we point out that aerosol particles affect other aspects of the ecosystem. Adverse effect of aerosols on ecosystems include deposition of acidic particles to poorly buffered soils and lakes, enhanced eutrophication of lakes and alpine regions by nitrate deposition, and the reduction of photosynthetic fluxes by heavy aerosol loadings downwind of industrial and urban centers. Aerosol particles also reduce visibility which results in transportation safety problems and aesthetic degradation (*Park et al.*, 2006; *Rokjin et al.*, 2006).

While aerosol particles are needed as seeds for the formation of cloud droplets, clouds formed in the presence of high number of particles have reduced precipitation efficiency. This leads to significant changes in ecosystem water transport and evapotranspiration (*Wang et al.*, 2008). Currently, the expansion of desert regions is thought to be caused by the inhibition of rainfall from such clouds. Such changes raise the potential for epidemic disease within certain ecosystems that could result in widespread amphibian extinctions (*Pounds et al.*, 2006).

The adverse health affects of aerosol particles are well documented (*Pope et al.*, 2000). Epidemiological studies show increased mortality due to cardiopulmonary disease and lung cancer in local and metropolitan environments with particulate mass concentrations persistently above ~10-20 μ g/m³ (*Dockery et al.*, 1993; *Pope et al.*, 2002; *and Symons et al.*, 2006). Further details of the health effects and descriptions of the challenges facing aerosol regulation are surveyed in Grahame and Schlesinger, (2007) and Peng et al., (2006).

1.4.2 Sources of Aerosol Particles

Aerosol particles originate from both natural and anthropogenic sources. Natural aerosol sources include sea spray, volcanic activity, terrestrial dust, and biomass burning (which in some instances qualify as an anthropogenic source). Particles are generally classified as primary or secondary based on their formation mechanism in the

atmosphere. Particles emitted directly into the atmosphere are called primary aerosol particles. Particles formed in the atmosphere from gas phase pre-cursors are called secondary aerosol particles. The formation of secondary aerosol particles is initiated by photo-oxidation reactions of the organic and inorganic gas phase species. Such reactions tend to lower the vapor pressure of the species which results in condensation onto existing particles or nucleation to form new particles.

Anthropogenic sources produce both primary aerosols and the gas phase precursors to secondary aerosols. Primary aerosol particles originate from industrial processes, the combustion of fossil fuels, non-industrial fugitive sources (i.e., construction work), and transportation sources (e.g., automobiles and trucks). A principle component of anthropogenic primary particles is black carbon (BC). Black carbon, also known as soot or elemental carbon, is a by-product of incomplete combustion. Black carbon particles typically have complex morphologies and unique optical properties. For these reasons, measurements of black carbon particles have become increasingly important toward increasing our knowledge of the radiative influence of the aerosol particle ensemble.

1.4.3 Aerosol Particles Atmospheric Lifetimes

The atmospheric lifetime of a particle is determined by the efficiency of the removal mechanisms acting on the particle. Particles are removed from the atmosphere by either dry or wet deposition. Therefore, the atmospheric lifetime of a particle is a function of the particle size, chemical composition, density, and surrounding meteorological conditions. Generally, atmospheric residence times for particles vary
from a few minutes to several weeks. This is to be contrasted to the residence time of greenhouse gases which have lifetimes of decades or longer. With much shorter residence times than greenhouse gases, aerosol particles present a unique measurement challenge to the atmospheric science community. That is, aerosol particles are not homogeneously distributed around a hemisphere or the globe. Instead, the number concentration, chemical composition, and size of particles are highly dependent on the source location and formation mechanism. Adding to this challenge, particles undergo physical and chemical transformations during their relatively short atmospheric lifetimes. Therefore, residence time is an important parameter for tracking important changes in the particle properties. Without understanding such changes, the effect of the aerosol particles on climate cannot be determined.

1.4.4 The Size of Atmospheric Aerosol Particles

Atmospheric particles are generally grouped into one of two size modes: coarse mode; particle diameters > 2.5 μ m and fine mode; particle diameters < 2.5 μ m. It is important to differentiate coarse and fine mode particles because particles within each of these modes typically originate from different sources and have different chemical, physical, and optical properties. Fine and coarse mode particles also undergo different atmospheric transformations, are removed from the atmosphere by different mechanisms, and subsequently have different influences on the ecosystem, visibility, human health, and climate.

Coarse mode particles contain a significant portion of the total mass of the aerosol ensemble but do not occur in large numbers (typically less than $\sim 1.0 \text{ p/cm}^3$ air) due to

their large sedimentation velocities causing them to have relatively short atmospheric lifetime. Coarse particles are produced through mechanical processes such as abrasive contact of machinery used in industrial and agricultural applications, entrainment of roadside dust from paved and unpaved roads, wind blown soil and biological particles, and sea spray. Because of their large size, coarse particles scatter more light than smaller atmospheric particles resulting in the reduction of visibility where coarse particle exist in the atmosphere.

Fine mode particles are categorized into two types: Aitken mode (0.01-0.1 μ m), and accumulation mode (0.01-2.5 μ m). Aitken mode particles account numerically for most of the aerosol particles but because of their small size, only a few percent of the total aerosol mass is in this particle mode (*Seinfeld and Pandis*, 2006).

Aitken mode particles are produced by vapor condensation during combustion processes and nucleation of low volatility gas phase species. Aitken mode particles are important for understanding new particle formation and growth in the atmosphere. Nucleation events have been observed in a variety of different environments including coastal, forested, rural, urban, and arctic regions arising from both natural and anthropogenic pre-cursor compounds (See *Zhang et al.*, 2005 and references therein). The atmospheric lifetime of Aitken mode particles is relatively short due to coagulation to form particles > 0.01 μ m, impaction onto surfaces, and evaporation (*Seinfeld and Pandis*, 2006). Because of their high number concentration and small size, Aitken mode particles are a potentially important source of cloud nuclei within continental atmospheres (*Kerminen et al.*, 2007). Continental atmospheres typically contain between 1,000 and 100,000 particles per cm³ of air with diameters between 0.1 μ m - 2.5 μ m. Particles within this size range are called accumulation mode particles because atmospheric removal mechanisms (dry and wet deposition) are relatively inefficient for particles of this size. As a result, the particles accumulate in the atmosphere over time. Typical mass loadings for accumulation mode particles range from 1-100 μ g/m³ (*Seinfeld and Pandis*, 2006).

Accumulation mode particles are typically formed in the atmosphere via coagulation of particles $< 0.1 \mu m$, emitted directly as primary particles from various combustion processes, or formed from secondary processes in the atmosphere. Because of their relatively long atmospheric lifetimes, accumulation mode particles undergo transport on regional and continental scales. During transport, physical and chemical transformations occur due to coagulation, gas-to-particle condensation, chemical reactions, and cloud processing. One of the main challenges when measuring aerosol particles is to accurately characterize the atmospheric transformations that are taking place. To quantify the direct and indirect radiative influences of ambient particles, the atmospheric processes that control the particle properties must be clearly understood.

1.4.5 The Challenge of Measuring Atmospheric Aerosol Particles

The chemical composition, size and structure of a given aerosol particle depends on the particle source, the amount of time the particle has spent in the atmosphere, the composition of the regional atmosphere, and the meteorological conditions of the region. At a given time and location, multiple sources contribute to the ambient aerosol ensemble. The number concentration, size, shape, and chemical composition of the particles are initially dependent on the nature of the source. Because particle sources are non-uniformly distributed, particles within the ambient ensemble often have different atmospheric residence times and have been exposed to varying degrees of atmospheric processing. To adequately characterize the particles and atmospheric processes that are taking place, measurements must be made in real-time with high spatial and temporal resolution. To obtain highly resolved spatial measurements, aerosol instrumentation must be portable and simple to maintain. As will be illustrated later, such instruments usually collect a large amount of data which need to be analyzed and interpreted. Reliable software programs must be written that provide a common analysis framework from which to inter-compare data sets from different regions. A comprehensive picture of the global aerosol distribution and atmospheric processes influencing the particle properties must be obtained.

1.5 SUMMARY OF THE CURRENT WORK

Relevant information about aerosol particles is obtained in field studies. Such studies have the advantage of providing measurements and observations of the real atmospheric system. However, under ambient conditions, a wide range of variables influences the aerosol properties. These variables continually change in the ambient atmosphere, further complicating our understanding of how the aerosol particles are transformed and how these transformations affect the climate forcing properties of the particles. Therefore, it is difficult to interpret field data and identify particle sources, transformations, and their radiative effects. Laboratory-based experiments can provide information that allows a more informed interpretation of the field data. Laboratory experiments are designed to more closely examine the influence of single, controlled variables on the particle properties of interest. In well designed laboratory experiments, conditions are kept as close as possible to those encountered in the ambient atmosphere. (Often this is a daunting task.) Ultimately, both laboratory and field measurements are necessary to understand the properties of aerosol particles and the atmospheric processes that transform these properties over time. As a result of combined lab and field-based observations, the accuracy of computational models of the climate system and projections of man-made climate change improve.

The work presented in this thesis focuses on instrumentation and measurements that provide information about the size, chemical composition, density, shape, and CCN activity of aerosol particles. Through the combination of instrument development, laboratory experiments and field measurements a more complete description of the mixing state and atmospheric transformations of aerosol particles is obtained. The chapters are organized as follows.

Chapter 2: Instrumental Methods.

The physical and chemical complexity of atmospheric aerosol particles necessitates the simultaneous use of multiple analytical techniques to understand particle properties. Chapter 2 summarizes the operating principles of the instrumental methods used in the current work with an emphasis on the combination of measurement techniques required to obtain a more complete characterization of the particles. The link between each instrument and measurements of size, chemical composition, density, shape, CCN activity, and mixing state is described.

Chapter 3: Particle Density Measurements using a Light Scattering Module with the Aerosol Mass Spectrometer.

To obtain single particle information from within the Aerodyne AMS instrument, a light scattering module was integrated into the Q-AMS system. The laboratory characterization of this new instrument combination (called LS-AMS) is described in Chapter 3. Results from the initial field deployment of the LS-AMS at Chebogue Point, Nova Scotia during the North East Air Quality Study (NEAQS-2004) are presented. Calibrations obtained during the laboratory experiments were used to enable single particle density measurements in the field. The LS-AMS provided details about the ambient ensemble mixing state and atmospheric transformations of the aerosol particles transported away from the Northeastern United States towards Europe.

Chapter 4: Single Particle Measurements during the MILAGRO Campaign in Mexico City.

The light scattering module was integrated into the second generation AMS instrument, equipped with a time-of-flight mass spectrometer. With the combined instrument (called LS-ToF-AMS), single particle mass spectra were triggered and saved based on the presence of a scattered light pulse. With this new instrument combination, a unique, quantitative approach to single particle mass spectrometry is achieved. The LS-ToF-AMS was deployed to Mexico City, Mexico in March of 2006 as part of the Megacity Initiative: Local and Global Research Observations (MILAGRO) field campaign. The single particle data provided detailed information about sources,

atmospheric processing and mixing state of the ambient aerosol ensemble ~ 40 km downwind of the city center.

Chapter 5. CCN activation studies.

The indirect effect of aerosol particles on climate remains the most uncertain of all radiative forcing components in the Earth-atmosphere system. In chapter 5 results from laboratory studies of CCN activation of ammonium sulfate, adipic acid, and soot particles are discussed. To determine the influence of atmospheric transformations on CCN activity, ammonium sulfate cores were coated with different organic materials of varying water solubility. Modified Kohler theory was used to model the two-component systems. The CCN activity of soot cores, coated with different water soluble compounds is also discussed.

Chapter 6: Intercomparison studies of black carbon.

Particles composed of black carbon (BC) or soot are directly emitted into the atmosphere as a result of incomplete combustion. Such particles are one of the dominant absorbers of solar radiation in the atmosphere. Given the ubiquitous nature of combustion as an energy source on the planet, black carbon particles are found throughout the atmosphere, especially in urban areas. Methods designed to measure black carbon have been recently developed that exploit different properties of the black carbon including incandescence or absorption. Such methods must be held to a common standard before the quantitative nature of the measurements is established. Two intercomparison studies of black carbon instruments have been conducted in the Boston

College laboratory. In Chapter 6, lessons learned from the 1^{st} intercomparison are outlined and improvements to the soot generation-sampling apparatus are summarized. Preliminary highlights from the 2^{nd} intercomparison study are provided.

1.6 SYMBOLS AND ABBREVIATIONS

The abbreviations and symbols used throughout the text are listed in Appendix A.

1.7 LIST OF PUBLICATIONS

- Chakrabarty, R.K., Moosmuller, H., Arnott, W.P., Garro, M.A., Slowik, J.G., Cross, E.S., Han, J.H., Davidovits, P., Onasch, T.B. & Worsnop, D.R. 2007, "Light scattering and absorption by fractal-like carbonaceous chain aggregates: Comparison of theories and experiment", *Applied Optics*, vol. 46, no. 28, pp. 6990-7006.
- Cross, E.S., Onasch, T.B., Canagaratna, M., Jayne, J.T., Kimmel, J., Yu, X.Y., Alexander, M.L., Worsnop, D.R. & and Davidovits, P. 2008, "Single Particle Characterization Using a Light Scattering Module Coupled to a Time-of Flight Aerosol Mass Spectrometer", *Submitted to ACPD*, .
- Cross, E.S., Onasch, T.B., Wrobel, W., Ahern, A., Jayne, J.T., Trimborn, A., Cappa, C., Schwarz, J., Lack, D., Olfert, J., Slowik, J., Massoli, P., Spackman, R., Brem, B., Worsnop, D.R. & and Davidovits, P. 2008, "Overview of the 2nd Boston College/Aerodyne Black Carbon Intercomparison Study", *In Preparation for ACPD*,
- Cross, E.S., Slowik, J.G., Davidovits, P., Allan, J.D., Worsnop, D.R., Jayne, J.T., Lewis, D.K., Canagaratna, M. & Onasch, T.B. 2007, "Laboratory and ambient particle density determinations using light scattering in conjunction with aerosol mass spectrometry", *Aerosol Science and Technology*, vol. 41, no. 4, pp. 343-359.
- Gao, R.S., Schwarz, J.P., Kelly, K.K., Fahey, D.W., Watts, L.A., Thompson, T.L.,
 Spackman, J.R., Slowik, J.G., Cross, E.S., Han, J.H., Davidovits, P., Onasch, T.B. &
 Worsnop, D.R. 2007, "A novel method for estimating light-scattering properties of

soot aerosols using a modified single-particle soot photometer", *Aerosol Science and Technology*, vol. 41, no. 2, pp. 125-135.

- Hings, S.S., Wrobel, W.C., Cross, E.S., Worsnop, D.R., Davidovits, P. & Onasch, T.B. 2008, "CCN activation experiments with adipic acid: effect of particle phase and adipic acid coatings on soluble and insoluble particles", *Atmospheric Chemistry and Physics*, vol. 8, no. 14, pp. 3735-3748.
- Slowik, J.G., Cross, E.S., Han, J.H., Davidovits, P., Onasch, T.B., Jayne, J.T., WilliamS, L.R., Canagaratna, M.R., Worsnop, D.R., Chakrabarty, R.K., Moosmuller, H., Arnott, W.P., Schwarz, J.P., Gao, R.S., Fahey, D.W., Kok, G.L. & Petzold, A. 2007, "An inter-comparison of instruments measuring black carbon content of soot particles", *Aerosol Science and Technology*, vol. 41, no. 3, pp. 295-314.
- Slowik, J.G., Cross, E.S., Han, J.H., Kolucki, J., Davidovits, P., Williams, L.R., Onasch, T.B., Jayne, J.T., Kolb, C.E. & Worsnop, D.R. 2007, "Measurements of morphology changes of fractal soot particles using coating and denuding experiments: Implications for optical absorption and atmospheric lifetime", *Aerosol Science and Technology*, vol. 41, no. 8, pp. 734-750.

1.8 REFERENCES FOR CHAPTER I

- Collins, W.D., Ramaswamy, V., Schwarzkopf, M.D., Sun, Y., Portmann, R.W., Fu, Q., Casanova, S.E.B., Dufresne, J.L., Fillmore, D.W., Forster, P.M.D., Galin, V.Y., Gohar, L.K., Ingram, W.J., Kratz, D.P., Lefebvre, M.P., Li, J., Marquet, P., Oinas, V., Tsushima, Y., Uchiyama, T. & Zhong, W.Y. 2006, "Radiative forcing by well-mixed greenhouse gases: Estimates from climate models in the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4)", *Journal of Geophysical Research-Atmospheres*, vol. 111, no. D14.
- Dockery, D.W., Pope, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G. & Speizer, F.E. 1993, "An Association between Air Pollution and Mortality in Six U.S. Cities 10.1056/NEJM199312093292401", *N Engl J Med*, vol. 329, no. 24, pp. 1753-1759.
- Grahame, T.J. & Schlesinger, R.B. 2007, "Health Effects of Airborne Particulate Matter: Do We Know Enough to Consider Regulating Specific Particle Types or Sources?", *Inhalation toxicology*, vol. 19, no. 6, pp. 457.

- Hinds, W.C. 1999, Aerosol technology: properties, behavior, and measurement of airborne particles, Wiley-Interscience, New York, NY, United States.
- Kerminen, V.M., Anttila, T., Petaja, T., Laakso, L., Gagne, S., Lehtinen, K.E.J. & Kulmala, M. 2007, "Charging state of the atmospheric nucleation mode: Implications for separating neutral and ion-induced nucleation", *Journal of Geophysical Research-Atmospheres*, vol. 112, no. D21.
- Kiehl, J.T. & Trenberth, K.E. 1997, "Earth's annual global mean energy budget", *Bulletin* of the American Meteorological Society, vol. 78, no. 2, pp. 197-208.
- Park, R.J., Jacob, D.J., Kumar, N. & Yantosca, R.M. 2006, "Regional visibility statistics in the United States: Natural and transboundary pollution influences, and implications for the Regional Haze Rule", *Atmospheric Environment*, vol. 40, no. 28, pp. 5405-5423.
- Peng, R.D., Dominici, F. & Zeger, S.L. 2006, "Reproducible epidemiologic research", *American Journal of Epidemiology*, vol. 163, no. 9, pp. 783-789.
- Pope, C.A. 2000, "Review: Epidemiological basis for particulate air pollution health standards", *Aerosol Science and Technology*, vol. 32, no. 1, pp. 4-14.
- Pope, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K. & Thurston, G.D. 2002, "Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution", *Jama-Journal of the American Medical Association*, vol. 287, no. 9, pp. 1132-1141.
- Pounds, J.A., Bustamante, M.R., Coloma, L.A., Consuegra, J.A., Fogden, M.P.L., Foster, P.N., La Marca, E., Masters, K.L., Merino-Viteri, A., Puschendorf, R., Ron, S.R., Sanchez-Azofeifa, G.A., Still, C.J. & Young, B.E. 2006, "Widespread amphibian extinctions from epidemic disease driven by global warming", *Nature*, vol. 439, no. 7073, pp. 161-167.
- Ramaswamy, V., Chanin, M.L., Angell, J., Barnett, J., Gaffen, D., Gelman, M., Keckhut,
 P., Koshelkov, Y., Labitzke, K., Lin, J.J.R., O'Neill, A., Nash, J., Randel, W., Rood,
 R., Shine, K., Shiotani, M. & Swinbank, R. 2001, "Stratospheric temperature trends: Observations and model simulations", *Reviews of Geophysics*, vol. 39, no. 1, pp. 71-122.

- Rokjin, J.P., Jacob, D.J., Kumar, N. & Yantosca, R.M. 2006, "Regional visibility statistics in the United States: Natural and transboundary pollution influences, and implications for the Regional Haze Rule", *Atmospheric Environment*, vol. 40, no. 28, pp. 5405-5423.
- Seinfeld, J.H. and Pandis, S.N. 2006, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, Inc., New York.
- Solomon, S., Qin, D., Manning, M., Marquis, M., Averyt, K., Tignor, M. & Miller, H.L.(. 2007, IPCC: Climate change 2007: The Scientific Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Symons, J.M., Wang, L., Guallar, E., Howell, E., Dominici, F., Schwab, M., Ange, B.A., Samet, J., Ondov, J., Harrison, D. & Geyh, A. 2006, "A case-crossover study of fine particulate matter air pollution and onset of congestive heart failure symptom exacerbation leading to hospitalization", *American Journal of Epidemiology*, vol. 164, no. 5, pp. 421-433.
- Wang, K.C., Dickinson, R.E. & Liang, S.L. 2008, "Observational evidence on the effects of clouds and aerosols on net ecosystem exchange and evapotranspiration", *Geophysical Research Letters*, vol. 35, no. 10.
- Zhang, Q., Canagaratna, M.R., Jayne, J.T., Worsnop, D.R. & Jimenez, J.L. 2005, "Timeand size-resolved chemical composition of submicron particles in Pittsburgh: Implications for aerosol sources and processes", *Journal of Geophysical Research-Atmospheres*, vol. 110, no. D7.

CHAPTER II

INSTRUMENTAL METHODS

2.1 OVERVIEW

The key measurements of particle size, chemical composition, density, shape, CCN activity, and mixing state featured in the current work require the simultaneous operation of a combination of instruments. In this chapter, the operating principles of each instrument and instrument combination are described.

The vaccum aerodynamic diameter (d_{va}) , mobility diameter (d_m) , and dynamic shape factor are three key parameters measured with the instruments described in this chapter.

The vacuum aerodynamic diameter (d_{va}) is defined as:

$$d_{va} = d_{ve} \frac{\rho_p}{\rho_0} \frac{1}{\chi}$$
(2-1)

Where d_{ve} is the volume equivalent diameter, defined as Volume = $\pi/6 d_{ve}^{3}$, ρ_{p} is the particle density, ρ_{0} is a normalizing density (1.00 g/cm³), and χ is the dynamic shape factor. Therefore, the vacuum aerodynamic diameter is a function of the size, shape, and density of the particle.

The dynamic shape factor is defined as:

$$\chi = \frac{\text{Drag on particle}}{\text{Drag on sphere of equal volume}}$$
(2-2)

As is evident from the definition (Eq. 2-2), $\chi = 1$ for a sphere and $\chi > 1$ for non-spherical particles.

The mobility diameter is defined as:

$$d_m = d_{ve} \frac{C_c(d_m)}{C_c(d_{ve})} \chi$$
(2-3)

Here, the $C_c(d)$ parameters are the Cunningham slip correction factors, which account for the reduced drag on a particle in the transition and free-molecular flow regimes (*Allen and Raabe* (1982, 1985a,b)).

In 2004, DeCarlo and Slowik presented the theoretical and experimental framework for determining the dynamic shape factor, fractal dimension, density, and composition of laboratory generated soot particles from simultaneous measurements of the mobility diameter and vacuum aerodynamic diameter (*DeCarlo et al.*, 2004 and *Slowik et al.*, 2004). Since that time, the system of equations have been used to study the morphological transformations of fractal soot particles coated with liquid and solid organics (*Slowik and Cross et al.*, 2007) and during the first inter-comparison study of black carbon instruments conducted at Boston College in May of 2005 (*Slowik and Cross et al.*, 2007). In the work presented here, the system of equations was used to provide information about the change in shape of coated soot particles in CCN activation studies (*Hings et al.*, 2008), as well as characterization of soot particles produced during the 2^{nd} intercomparison study of black carbon instruments conducted at Boston College in July of 2008 (*Cross et al.*, 2008).

2.2 INSTRUMENT DESCRIPTIONS

The measurements used in the current work include: (1) Combined optical and vacuum aerodynamic diameter measurements to yield particle density and mixing state

information (*Cross et al.*, 2007; *Cross et al.*, 2008a), (2) Combined mobility and vacuum aerodynamic diameter measurements to yield particle shape, fractal dimension, and chemical composition (*Slowik et al.*, 2004, *DeCarlo et al.*, 2004, *Slowik and Cross et al.*, 2007, *Slowik and Cross et al.*, 2007), and (3) Combined measurements of chemical composition, CCN activity, mobility diameter, and vacuum aerodynamic diameter to determine the influence of particle shape and composition on CCN activity (*Hings et al.*, 2008).

An additional feature of the current work includes the development and characterization of a stable hydrocarbon combustion source for use in laboratory studies of soot particles (*Wrobel*, 2008; *Cross et al.*, 2008b).

2.2.1 Combined Optical and Vacuum Aerodynamic Diameter Measurements

The Aerodyne Aerosol Mass Spectrometer (AMS) is the central instrument used in the laboratory and field studies discussed in this thesis. A major component of the research presented here is the development, characterization, and use of a light scattering module integrated into the AMS. One advantage of the internal light scattering module is that for every particle that scatters sufficient light for detection, an optical and vacuum aerodynamic diameter are obtained. As will be discussed in greater detail in the following sections, the combination of optical and vacuum aerodynamic diameters provides a real-time, single particle measure of the effective density (ρ_{eff}). Measurements of single particle densities yield valuable information about the mixing state and atmospheric transformations of the ambient aerosol ensemble.

2.2.1.1 Aerodyne Aerosol Mass Spectrometer (AMS)

A schematic of the AMS is shown in Figure 2-1. The AMS has been described in detail in other publications (Javne et al. 2000; Jiménez et al. 2003; Drewnick et al. 2005; and DeCarlo et al. 2006); here we provide a brief overview of the instrument. The AMS consists of three main sections: (1) aerodynamic inlet, (2) time of flight region (dimensions shown) and (3) particle vaporizer and mass spectrometer. Particles enter the AMS through a 100 µm orifice and pass through a series of aerodynamic lenses. In their passage through the inlet, particles are accelerated by the pressure drops and are focused into a narrow beam that passes through the time of flight region of the instrument. The particles then impact a heated surface where the non-refractory components of the particle are vaporized at $T \sim 600^{\circ}$ C. The non-refractory chemical composition is measured by ionizing the vapor plume via electron impact (~70 eV), and characterizing the chemical constituents with a mass spectrometer. The AMS detection process has sufficient sensitivity and time response to detect single particle vaporization events occurring on a $\sim 100 \ \mu s$ time scale which is fast compared to the particle time-of-flight (approximately 5 ms). The aerosol mass loadings (in μ g/m3) for identified chemical species are obtained by summing the ion signals in the mass spectrum and using instrument calibrations of the ionization and collection efficiencies for each species.



Figure 2-1. Schematic of the LS-AMS.

The AMS directly measures two critical properties of the aerosol particles: (1) the vacuum aerodynamic diameter and (2) the non-refractory chemical composition. These measurements are obtained by alternately operating the instrument between two data acquisition modes: (1) Particle Time-of-Flight (PToF) mode and (2) Mass Spectrum (MS) mode.

In the PToF mode, a spinning chopper wheel ($\sim 120 \text{ Hz}$) with a 1% slit modulates the particle beam. Typical ambient particle number concentrations (5,000-8,000 p/cm³) result in a single particle entering the time-of-flight chamber 95% of the time. Single particles enter the time-of-flight chamber and the particle velocity is based on the timeof-flight between the chopper opening and time of a chemical ion signal at the vaporizer. As shown in Figure 2-1, the light scattering module is located within the time-of-flight region of the AMS, 0.130 m ahead of the vaporizer surface. Light scattering data are acquired while operating the instrument in PToF mode. The light scattering pulses provide an additional (and more accurate) measure of the particle velocity based on the time-of-flight between the chopper opening and the laser beam.

In the MS mode, an ensemble average mass spectrum is obtained by alternately blocking and opening the particle beam and calculating a difference mass spectrum. (The subtraction eliminates the effect of background signal in the mass spectrometer.)There is no particle size information available while running in MS Mode.

The original version of the AMS used a quadrupole mass spectrometer for chemical ion detection (Q-AMS - shown schematically in Figure 2-1 and described in *Jayne et al.*, 2000). In more recent versions of the AMS, the quadrupole mass spectrometer has been replaced with a time-of-flight mass spectrometer (ToF-AMS - shown schematically in Figure 2-2 and described in *Drewnick et al.*, 2005 and *DeCarlo et al.*, 2006).



Figure 2-2. Schematic of the LS-ToF-AMS.

The key difference between the ToF-AMS and Q-AMS instruments is the time necessary to acquire a full mass spectrum. In the case of the quadrupole, a full scan (10-300 amu) takes approximately 300 ms. With the time-of-flight mass spectrometer, a full mass spectrum is obtained in approximately 12 µs. Typically, the particle time-of-flight from the chopper to the vaporizer surface is 4-5 ms. Therefore, in PToF mode, the ToF-AMS is capable of measuring full mass spectra for single particles whereas the Q-AMS is limited to analyzing a single m/z signal over the time required for single particle detection. Light scattering modules have been integrated into both Q-AMS and ToF-AMS systems. The general components of the light scattering module are described in the following section. The unique advantages of having the light scattering module integrated with the Q-AMS (called LS-AMS) and ToF-AMS (called LS-ToF-AMS) are described in detail in Chapters 3 and 4 respectively.

2.2.1.2 Light Scattering Module

A simplified schematic of the light scattering module is shown in Figure 2-3. The module is comprised of five principle components: a diode pumped 405 nm continuous wave 50 mW laser (CrystaLaser, LC BCL-050-405), external mirrors for alignment of the light beam, an ellipsoidal mirror for scattered light collection (Opti-Forms E103-2-01), a razor blade beam stop for quenching the throughput laser light, and a photomultiplier tube (PMT) for light detection (Hamamatsu H6779-00). The spurious scattered light is reduced by a series of apertures along the laser beam (x) axis identified in Figure 2-3. The laser beam axis is oriented perpendicular to the particle beam axis (z-axis) and the intersection point between the laser and particle beams is centered at one focal point of the ellipsoidal mirror, while the active surface of the PMT is mounted at the second focal point. A 15 k Ω resistor terminates the output of the PMT, and the output pulses are transmitted to the computer via an ADC board (National Instruments).



Figure 2-3. Components and Orientation of Light Scattering Module

The main difference between the optical detection method used in the LS-AMS system and optical sizing techniques previously employed (*Murphy et al.* 2004; *Salt et al.* 1996; *Dutcher* 2004; *Moffet et al.* 2005) is in the diameter of the laser beam. In the LS-AMS, the laser beam is diverging at the intersection with the particle beam whereas in other cited systems the laser beam is tightly focused. In Figure 2-3, the particle beam is displayed as a solid dot, along the z-axis (into and out of the paper), perpendicular to the laser beam axis. With a broad laser beam (~2.7 mm in diameter along the y axis) nearly all particles that impact the vaporizer first pass through the laser beam. Therefore, the LS-AMS system, via the optical scattering signals, detect all particles that impact the surface of the vaporizer if they are larger than the optical size detection limit ($d_p \ge 180$ nm).

2.2.2 Differential Mobility Analyzer (DMA)

The DMA (also known as an electrostatic classifier) is the most commonly used instrument to measure particle size (Knutson and Whitby, 1975a,b). The DMA classifies particles as a function of their electrical mobility diameter (d_m) which is the diameter of a sphere with the same migration velocity in constant electric field as the particle of interest (DeCarlo et al., 2004). In the DMA, a polydisperse size distribution of particles is passed through a Krypton-85 source. The source produces both positive and negative air ions that are attracted to the oppositely charged particles. This results in an equilibrium charge distribution centered on particles with zero charge with a smaller fraction of particles containing $\pm 1, 2, \text{ or } 3$ elementary charges. The configuration of the DMA, after the neutralizer, consists of a hollow, grounded cylinder with a concentric charged rod. The polydisperse distribution of particles enters the top of the column and combines with a sheath flow of particle-free air. The sheath flow is typically set to be approximately 10 times the polydisperse aerosol flow. The sheath and polydisperse aerosol flow travel axially between the charged rod and the inner wall of the column. Near the bottom of the column a slit is cut into the central rod allowing a fraction of the particles to exit the instrument. The transmitted particles are size-selected based on their electrical mobility. The electrical mobility of the particles refers to the steady-state migration velocity of the particle per unit electric field strength. By varying the voltage of the central rod and the subsequent strength of the electric field, particles of different mobilities (i.e., sizes) can be selected for different voltage settings.

2.2.3 Condensation Particle Counters (CPC)

Condensation particle counters (CPC, e.g. TSI model 3010, TSI Inc., Shoreview, MN, USA) provide a continuous measure of the total number concentration in particles/cm³ air (p/cm³) of particles sampled above a certain size (typically $d_p > 0.010$ $\mu m = 10$ nm). Particles smaller than 10 nm are not easily detected. The principle of the CPC is to grow the particles by condensation to a size that is optically detected. In the CPC particles are passed through a supersaturated reservoir (often several hundred percent supersaturation) containing either water or n-butyl alcohol. The vapor condenses onto the particles with growth factors of 100-1000 resulting typically in 10 µm diameter droplets. The droplets pass through a laser beam where they are then optically detected and counted. The high supersaturations used in the CPC make the instrument insensitive to the chemical composition differences. The vapor pressure of the fluid used to grow the particles must be (1) high enough to allow condensational growth to 10 μ m droplets in ~ 0.3 s of exposure time and (2) low enough to ensure that the gas flow through the instrument is not dominated by the condensable material. Different CPCs will have different minimum size detection limits and size-dependent collection efficiencies.

2.2.4 Scanning Mobility Particle Sizer (SMPS)

When operated in series, the DMA and CPC measure the mobility diameter size distribution of the particles. As discussed above, the voltage applied to the central rod within the DMA permits particles of a given mobility to be transmitted through the DMA column. As the voltage is changed, the size of the transmitted particles also changes. In an SMPS, the DMA column voltage is scanned while the CPC continuously monitors the

total number concentration at each voltage. In this way, the size distribution of the sampled particles can be obtained. In the laboratory experiments presented here, two DMA's were used. The first DMA size selected a single size from a polydisperse distribution of particles produced by a source, while the second DMA (coupled to a CPC and used as an SMPS) scanned the distribution providing a mobility diameter distribution of the size-selected particles and detected changes in size as a result of particle conditioning after the first DMA.

2.2.5 Combined CCN and SMPS-AMS Measurements

The CCN activity of aerosol particles depends on the particle size, shape, and chemical composition. Therefore, when conducting CCN studies a combination of instruments must be used to characterize the particles properties of interest. A Cloud Condensation Nuclei counter (CCN, Droplet Measurement Technologies, Boulder, CO, USA) has been combined with the SMPS-AMS system to characterize the influence of particle size, shape and chemical composition on the CCN activity of coated and uncoated particles (*Hings et al.*, 2008). The operational details of the CCN instrument are presented in this chapter. The improved soot source was used to study the influence of particle morphology and chemical composition on the CCN activity of coated soot particles. Results from CCN studies of coated and uncoated particles are presented in Chapter 5.

2.2.5.1 Cloud Condensation Nuclei Counter (CCNC)

The Cloud Condensation Nuclei Counter (CCNC, Droplet Measurement Technologies, Boulder, CO) used in the current work was operated in a continuous flow mode. That is, the instrument provided fast sampling by continually monitoring the CCN activity of the particles passing through it. The instrument was capable of generating nearly constant values of supersaturation between 0.07% and 3.7% which brackets atmospheric conditions. The stated accuracy, by the manufacturer, of these supersaturation values is $\pm 2\%$. Supersaturation was easily controlled and maintained, making it possible to scan the full range of supersaturations for a given particle size.

A schematic of the CCNC is shown in Figure 2-4. The aerosol flow introduced into the CCNC instrument is split into an aerosol and a sheath flow. The sheath flow is filtered (to remove the aerosol particles), humidified and heated. This sheath flow constrains the main aerosol flow to the centerline of the cylindrical CCNC column. The inner wall of the column is continually wetted and a positive temperature gradient dT is applied to the column in the direction of the flow. Water vapor supersaturation is therefore generated along the centerline of the column (due to the difference in diffusion rates between water and heat). Particles begin to grow at the point when the supersaturation inside the instrument is equal to the critical supersaturation, S_c . Droplets that grow to diameters larger than 1 µm are detected by an optical particle counter (OPC) at the exit of the column and are defined as CCN-active particles.

The supersaturation in the CCNC column is primarily a function of the temperature difference (dT) between the top (upstream) and the bottom (downstream) of the CCNC column. It also depends on the flow and the pressure inside the instrument. The relationship between supersaturation (*S*) and the measured temperature difference

(dT) inside the CCN column is determined by calibration with ammonium sulfate particles at a specific flow and pressure. The CCN activity of ammonium sulfate particles of known size (d_m) is used as the calibration standard. To obtain reliable experimental results, the CCNC apparatus must to be carefully calibrated in each application. Detailed descriptions of the CCNC and its calibration have been described (*Roberts and Nenes*, 2005, *Lance et al.*, 2006, and *Rose et al.*, 2008).



Figure 2-4. Schematic of the DMT CCNC instrument (Roberts and Nenes, 2005).

2.3 LABORATORY SOOT SOURCE

The key feature of the black carbon experiments conducted at Boston College is the soot generation system. In the current work, the stability of the soot generation/sampling system has been improved through modifications to the sampling interface (*Wrobel*, 2008; *Cross et al.*, 2008). A description of the soot generationsampling system and modifications to the system are provided in Chapter 6. The improved soot source was used in the most recent inter-comparison study of black carbon instruments, results from which are summarized in Chapter 6.

2.4 REFERENCES FOR CHAPTER II

- Allen, M.D. & Raabe, O.G. 1985, "Slip correction measurements for aerosol particles of doublet and triangular triplet aggregates of spheres", *Journal of Aerosol Science*, vol. 16, no. 1, pp. 57-67.
- Allen, M.D. & Raabe, O.G. 1985, "Slip correction measurements of spherical solid aerosol particles in an improved Millikan apparatus", *Aerosol Science and Technology*, vol. 4, no. 3, pp. 269-286.
- Allen, M.D. & Raabe, O.G. 1982, "Re-evaluation of Millikan oil drop data for the motion of small particles in air", *Journal of Aerosol Science*, vol. 13, no. 6, pp. 537-547.
- Baron, P.A. 2001, "Measurement of airborne fibers: A review", *Industrial health*, vol. 39, no. 2, pp. 39-50.
- Cross, E.S., Onasch, T.B., Canagaratna, M., Jayne, J.T., Kimmel, J., Yu, X.Y., Alexander, M.L., Worsnop, D.R. & and Davidovits, P. 2008, "Single Particle Characterization Using a Light Scattering Module Coupled to a Time-of Flight Aerosol Mass Spectrometer", *Submitted to ACPD*, .

- Cross, E.S., Onasch, T.B., Wrobel, W., Ahern, A., Jayne, J.T., Trimborn, A., Cappa, C., Schwarz, J., Lack, D., Olfert, J., Slowik, J., Massoli, P., Spackman, R., Brem, B., Worsnop, D.R. & and Davidovits, P. 2008, "Overview of the 2nd Boston College/Aerodyne Black Carbon Intercomparison Study", *In Preparation for ACPD*,
- Cross, E.S., Slowik, J.G., Davidovits, P., Allan, J.D., Worsnop, D.R., Jayne, J.T., Lewis, D.K., Canagaratna, M. & Onasch, T.B. 2007, "Laboratory and ambient particle density determinations using light scattering in conjunction with aerosol mass spectrometry", *Aerosol Science and Technology*, vol. 41, no. 4, pp. 343-359.
- DeCarlo, P.F., Kimmel, J.R., Trimborn, A., Northway, M.J., Jayne, J.T., Aiken, A.C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K.S., Worsnop, D.R. & Jimenez, J.L. 2006, "Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer", *Analytical Chemistry*, vol. 78, no. 24, pp. 8281-8289.
- DeCarlo, P.F., Slowik, J.G., Worsnop, D.R., Davidovits, P. & Jimenez, J.L. 2004, "Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory", *Aerosol Science and Technology*, vol. 38, no. 12, pp. 1185-1205.
- Drewnick, F., Hings, S.S., DeCarlo, P., Jayne, J.T., Gonin, M., Fuhrer, K., Weimer, S., Jimenez, J.L., Demerjian, K.L., Borrmann, S. & Worsnop, D.R. 2005, "A new timeof-flight aerosol mass spectrometer (TOF-AMS) - Instrument description and first field deployment", *Aerosol Science and Technology*, vol. 39, no. 7, pp. 637-658.
- Dutcher, D.D. 2004, Optical Sizing of Particles using the Aerosol Time of Flight Mass Spectrometer A Mechanical Engineering Plan B Master's Degree Paper, University of Minnesota.
- Hinds, W.C. 1999, Aerosol technology: properties, behavior, and measurement of airborne particles, Wiley-Interscience, New York, NY, United States.
- Hings, S.S., Wrobel, W.C., Cross, E.S., Worsnop, D.R., Davidovits, P. & Onasch, T.B. 2008, "CCN activation experiments with adipic acid: effect of particle phase and adipic acid coatings on soluble and insoluble particles", *Atmospheric Chemistry and Physics*, vol. 8, no. 14, pp. 3735-3748.

- Jayne, J.T., Leard, D.C., Zhang, X.F., Davidovits, P., Smith, K.A., Kolb, C.E. & Worsnop, D.R. 2000, "Development of an aerosol mass spectrometer for size and composition analysis of submicron particles", *Aerosol Science and Technology*, vol. 33, no. 1-2, pp. 49-70.
- Jimenez, J.L., Jayne, J.T., Shi, Q., Kolb, C.E., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., Zhang, X.F., Smith, K.A., Morris, J.W. & Davidovits, P. 2003, "Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer", *Journal of Geophysical Research-Atmospheres*, vol. 108, no. D7.
- Knutson, E. & Whitby, K. 1975, "Accurate Measurement of Aerosol Electric Mobility Moments", *Journal of Aerosol Science*, vol. 6, pp. 453-460.
- Knutson, E. & Whitby, K. 1975, "Aerosol Classification by Electric Mobility: Apparatus, Theory, and Applications", *Journal of Aerosol Science*, vol. 6, pp. 443-451.
- Lance, S., Medina, J., Smith, J.N. & Nenes, A. 2006, "Mapping the operation of the DMT Continuous Flow CCN counter", *Aerosol Science and Technology*, vol. 40, no. 4, pp. 242-254.
- Meakin, P. 1988, "Fractal Aggregates", *Advances in Colloid and Interface Science*, vol. 28, no. 4, pp. 249-331.
- Moffet, R.C. & Prather, K.A. 2005, "Extending ATOFMS measurements to include refractive index and density", *Analytical Chemistry*, vol. 77, no. 20, pp. 6535-6541.
- Murphy, D.M., Cziczo, D.J., Hudson, P.K., Schein, M.E. & Thomson, D.S. 2004, "Particle density inferred from simultaneous optical and aerodynamic diameters sorted by composition", *Journal of Aerosol Science*, vol. 35, no. 1, pp. 135-139.
- Park, K., Cao, F., Kittelson, D.B. & McMurry, P.H. 2003, "Relationship between particle mass and mobility for diesel exhaust particles", *Environmental science & technology*, vol. 37, no. 3, pp. 577-583.
- Roberts, G.C. & Nenes, A. 2005, "A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements", *Aerosol Science and Technology*, vol. 39, no. 3, pp. 206-221.
- Rose, D., Gunthe, S.S., Mikhailov, E., Frank, G.P., Dusek, U., Andreae, M.O. & Poschl, U. 2008, "Calibration and measurement uncertainties of a continuous-flow cloud

condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment", *Atmospheric Chemistry and Physics*, vol. 8, no. 5, pp. 1153-1179.

- Salt, K., Noble, C.A. & Prather, K.A. 1996, "Aerodynamic particle sizing versus light scattering intensity measurement as methods for real time particle sizing coupled with time-of-flight mass spectrometry", *Analytical Chemistry*, vol. 68, no. 1, pp. 230-234.
- Slowik, J.G. 2006, Morphology, Composition, and Atmospheric Processing of Soot Particles, Boston College.
- Slowik, J.G., Cross, E.S., Han, J.H., Davidovits, P., Onasch, T.B., Jayne, J.T., WilliamS, L.R., Canagaratna, M.R., Worsnop, D.R., Chakrabarty, R.K., Moosmuller, H., Arnott, W.P., Schwarz, J.P., Gao, R.S., Fahey, D.W., Kok, G.L. & Petzold, A. 2007, "An inter-comparison of instruments measuring black carbon content of soot particles", *Aerosol Science and Technology*, vol. 41, no. 3, pp. 295-314.
- Slowik, J.G., Cross, E.S., Han, J.H., Kolucki, J., Davidovits, P., Williams, L.R., Onasch, T.B., Jayne, J.T., Kolb, C.E. & Worsnop, D.R. 2007, "Measurements of morphology changes of fractal soot particles using coating and denuding experiments: Implications for optical absorption and atmospheric lifetime", *Aerosol Science and Technology*, vol. 41, no. 8, pp. 734-750.
- Slowik, J.G., Stainken, K., Davidovits, P., Williams, L.R., Jayne, J.T., Kolb, C.E., Worsnop, D.R., Rudich, Y., DeCarlo, P.F. & Jimenez, J.L. 2004, "Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 2: Application to combustion-generated soot aerosols as a function of fuel equivalence ratio", *Aerosol Science and Technology*, vol. 38, no. 12, pp. 1206-1222.
- Wang, G.M. & Sorensen, C.M. 1999, "Diffusive mobility of fractal aggregates over the entire knudsen number range", *Physical Review E*, vol. 60, no. 3, pp. 3036-3044.
- Wrobel, W. 2008, Exploring the Role of Particulate Matter in Global Warming, Boston College.

CHAPTER III

PARTICLE DENSITY MEASUREMENTS USING A LIGHT SCATTERING MODULE COUPLED TO AN AEROSOL MASS SPECTROMETER

3.1 OVERVIEW

Real-time density determination often requires the use of multiple instruments. This factor makes real-time density determination particularly challenging during field measurement campaigns. To address the need for instrumentation capable of measuring density from a single operating platform, a light scattering module was integrated into the AMS (LS-AMS). The objective of this chapter is to describe the technical details and measurement capabilities of the LS-AMS system through laboratory and ambient aerosol The chapter begins with a summary of current particle density measurements. measurements used in the field. The operating principles of the LS-AMS are then described in the context of these other techniques. Results from the laboratory characterization of the LS-AMS method are then provided, including a quantitative analysis of the measurement uncertainties associated with this new method of density determination. In the final section of the chapter, results are presented from the field deployment of the LS-AMS system to Chebogue Point, Nova Scotia which was part of the Northeast Air Quality Study (NEAQS-2004). The ability of the LS-AMS system to provide real-time density determination for the ambient aerosol ensemble is illustrated. The extension of the LS-AMS method to determine the mixing state of the ambient aerosol ensemble is discussed.

The material presented in this chapter was published as Cross, E.S., Slowik, J.G., Davidovits, P., Allan, J.D., Worsnop, D.R., Jayne, J.T., Lewis, D.K., Canagaratna, M. & Onasch, T.B. 2007, "Laboratory and ambient particle density determinations using light scattering in conjunction with aerosol mass spectrometry", *Aerosol Science and Technology*, vol. 41, no. 4, pp. 343-359.

3.2 BACKGROUND SUMMARY OF PARTICLE DENSITY MEASUREMENTS

The influence of atmospheric aerosol particles on both regional and local climate depends on aerosol composition, size, shape, density, and number concentration (*Seinfeld and Pandis, 2006; Ramanathan et al., 2001; Lohmann and Lesins 2005*). For effective modeling of climate forcing by aerosols, accurate knowledge of these properties is needed. Such knowledge requires routine and broad-based monitoring of aerosols.

The real-time determination of aerosol particle density is particularly important. For example, through real-time density determination, number distributions can be converted to mass or volume distributions (*McMurry et al.*, 2002). Likewise, density relates the aerodynamic diameter to the Stokes diameter which, in the case of a compact sphere, is equal to the geometric diameter. Density also provides the connection between the electric mobility diameter and aerodynamic diameter both of which are routinely measured with available instrumentation (*DeCarlo et al.*, 2004).

The density of aerosol particles will change as a result of chemical and physical processing as they are transported through the atmosphere. For example, it has been shown that the density of humic-like substances (HULIS) increases due to oxidation with atmospheric lifetime (*Dinar et al.*, 2006). Similarly, it is likely that the density of urban organic aerosols increases due to oxidation of hydrocarbons during their atmospheric residence time (*Turpin and Lim* 2001). It is thus evident that measurements of aerosol density as a function of time and location provide key information about atmospheric processing. Such information yields data required to classify aerosol emission sources and to determine source apportionment.

While the basic definition of density is simple, (particle mass/particle volume), the irregular shape and complex composition of aerosol particles make actual real-time determination of density challenging. Particle morphology (shape and structure), size, composition, and phase must be considered when determining aerosol density from available measurable parameters. To take into account the aerosol complexity, the concept of "effective" (sometimes called "apparent") density (ρ_{eff}) has been introduced (*Baron et al.*, 2001; *Hand et al.*, 2002; *McMurry et al.*, 2002; *Jimenez et al.*, 2003). The definition of effective density depends on the measurement technique as discussed by DeCarlo et al., (2004) and is a function of the actual particle density (ρ_p) and the particle dynamic shape factor (χ) (See equation 3-3)). (The dynamic shape factor takes into account deviations from spherical shape. It is unity for a sphere and is usually greater than one for non-spherical particles.) The effect of particle morphology on ρ_{eff} is likewise discussed by DeCarlo et al., (2004).

For non-spherical particles of unknown shape factor (χ) and complex but known composition and no internal voids, the three parameters particle mass (m_p), electrical mobility diameter (d_m), and aerodynamic diameter (d_a) yield the particle density ρ_p (*Kelly and McMurry* 1992; *DeCarlo et al.*, 2004). For such non-spherical particles any two of these parameters yield ρ_{eff} .

The relationships between the three parameters m_p , d_m , and d_a are such that if one knows or assumes that the particles are spherical, particle density can be determined from two of the three measurable parameters (*DeCarlo et al.*, 2004). For spherical particles, the mobility diameter is equal to the physical diameter (d_p) of the particle. The electrical mobility diameter is defined as the diameter of a sphere that has the same migration velocity in a constant electric field as the particle of interest. The aerodynamic diameter is defined as the diameter of a sphere with standard density that settles at the same terminal velocity as the particle of interest. As discussed in greater detail below d_a depends on the flow regime surrounding the particle.

3.2.1 Instruments used for measuring the density parameters

Typically, different instruments are required to measure each of the parameters m_p , d_m , and d_a . The particle mass can be measured physically or chemically. Physical measurements of particle mass are made with standard gravitational methods using filters, Tapered Element Oscillating Microbalances (TEOM), or aerosol particle mass analyzers (APM) including the Couette centrifugal particle mass analyzer (CPMA). Chemical measurements of the particle mass can be obtained with a Micro-Orifice Uniform Deposit Impactor (MOUDI) or calibrated aerosol mass spectrometers such as an AMS.

The mobility diameter (d_m) is measured with instruments such as a differential mobility analyzer (DMA) or scanning mobility particle sizer (SMPS) (See section 2.2.2.1). As discussed in DeCarlo et al., 2004, the type of aerodynamic diameter (d_a) measured depends upon the flow regime of the gas around the particle. Aerodynamic diameters measured in the continuum regime are denoted as d_{ca} while those measured in the freemolecular regime are referred to as vacuum aerodynamic diameters, denoted d_{va} . The aerodynamic particle sizer (APS) is an example of an instrument that provides a measure of d_{ca} . Here the particle time-of-flight is obtained by accelerating the particles in a gas jet at ambient pressure (*Ananth and Wilson* 1988; *Brockmann and Radar* 1990). Aerosol mass spectrometers that utilize a low-pressure (~1.5 Torr, 200 Pa) aerodynamic inlet or a converging nozzle, measure the particle d_{va} . This includes: the aerosol time-of-flight mass spectrometer (ATOFMS) (*Prather et al.*, 1994), the single particle laser ablation time-offlight mass spectrometer (SPLAT-MS) (*Zelenyuk and Imre* 2005), and the AMS (*Jayne et al.*, 2000). For high altitude (~ 40 mbar) aircraft sampling of aerosol particles, the particle analysis by laser mass spectrometry instrument (PALMS) (*Murphy and Thomson* 1995) also measures the particle d_{va} . These types of instruments offer the distinct advantage of simultaneously obtaining physical (d_{va}) and chemical (mass spectra) information on the same particles (for a recent review of online aerosol instrumentation see *Sullivan et al.*, 2005).

Studies that utilized the combination of two physical measurements to yield particle density include those of Kelly and McMurry (1992) and Schleicher et al., (1995) who used a DMA to measure d_m and an impactor in conjunction with a particle concentration measurement to obtain m_p . McMurry et al., (2002) used an APM developed by Ehara et al., (1996) along with a TDMA (Tandem Differential Mobility Analyzer) system, to measure the effective density of ambient urban aerosol particles. Khlystov et al., 2004 developed an algorithm for combining SMPS and APS size distributions. This algorithm was tested by comparing size distributions measured using a MOUDI cascade impactor and mass concentrations measured with a PM_{2.5} TEOM. More recently, Geller et al., (2006) used the DMA-APM method of McMurry to perform effective density measurements of ambient aerosol particles at several California sites.

When coupled to a DMA apparatus, aerosol mass spectrometers can measure the particle density from the relationship between d_m and d_{va} (See section 2.2.2). The SPLAT-
MS instrument has been used in this way to make high precision density measurements of spherical laboratory generated particles (*Zelenyuk et al.*, 2005) and effective density measurements on non-spherical laboratory particles (*Zelenyuk et al.*, 2006a). In our previous studies, we obtained particle densities using the combination of a DMA to select d_m and an Aerodyne aerosol mass spectrometer (AMS) to measure d_{va} , obtained from the particle time-of-flight within the AMS, and m_p , measured with the calibrated AMS (As described in section 2.2.2 and in *DeCarlo et al.*, 2004 and *Slowik et al.*, 2004). The DMA-AMS system has been utilized to measure the density of fractal soot particles (*DeCarlo et al.*, 2004; *Slowik et al.*, 2004) as well as changes in the density of spherical particles undergoing heterogeneous chemical reactions (*Katrib et al.*, 2005). For these studies, particle densities were determined from the average size (d_m and d_{va}) distributions of ensembles of well-defined laboratory aerosol particles.

3.2.2 Optical Sizing Measurements

In the above experiments, the physical particle size (d_m) was obtained via measurement of particle mobility. It is possible to obtain a measure of particle size from calibrated optical scattering signals as was demonstrated by Hand et al., (2002). In their experiment, the particle flow was split. Optical scattering by the particles was measured with an optical particle counter (OPC) in one branch and d_a (specifically d_{ca}) was measured in the other branch using an Aerodynamic Particle Sizer (APS). These two separate ensemble average measurements provided the information necessary for effective density determination. Murphy et al., (2004) was one of the first to emphasize the advantage of measuring the optical and aerodynamic diameters of individual particles within a traditional aerodynamic sizing instrument. In their field study, the optical scattering pulse heights generated from particles within the time-of-flight region of a PALMS instrument were used in combination with the measured aerodynamic diameter to estimate particle density. They found that the average density measurement based on the optical and aerodynamic diameters was consistent with the density inferred from the chemical mass spectra. Salt et al., (1996) provided an assessment of the simultaneous measurements of scattered light intensity (collected at a single angle) and aerodynamic size with the ATOFMS. It was found that reliable optical sizing of the particles was not possible due to signal-to-noise constraints. Expanding on the earlier work of Dutcher et al., (2004), Moffet et al (2005) measured scattered light intensity and d_{va} of laboratory aerosol particles using an ATOFMS. Via an absolute calibration of the collection optics, refractive index and density of the sampled particles was determined.

3.2.3 Real-Time Density Determination with a LS-AMS

In this chapter, a recently developed light scattering (LS) module integrated into the AMS (LS-AMS) is described. The central feature of this technique is that for every particle greater than the light scattering detection limit (~180 nm) that enters the AMS the magnitude of the scattered light signal (R_{LS}) and the vacuum aerodynamic diameter (d_{va}) are determined. The scattered light signal yields an optical diameter (d_o). In this way, the LS-AMS instrument can determine two diameters, d_o and d_{va} for the same particle. Particle density can be determined from these two diameter measurements assuming the particles are spherical. In addition to the physical parameters, d_o and d_{va} , the quantitative chemical composition of the aerosol particles is measured with the LS-AMS. This allows one to compare the physically derived density (from d_o and d_{va}) with the chemically derived density (from m_p). In addition to the density information, the particle by particle light scattering signal provides an *in-situ* measurement of the collection efficiency of the AMS.

The LS-AMS uses a different approach to optical scattering than the systems used by Murphy et al., (2004) and Moffet et al., (2005). The LS-AMS uses a diverging laser beam to intercept all of the particles focused by the aerodynamic inlet. The broad laser beam and aerodynamic focusing provides two advantages: (1) Deviations in scattered light signal as a function of different particle trajectories through the laser beam are minimized. Thus, the broad laser beam enables more accurate correlation between the scattered light intensity and particle size. (2) The vaporization efficiency of the AMS can be measured because all particles that strike the vaporizer first cross the laser beam and are optically detected ($d_p > 180$ nm).

Here, we describe the calibration and operation of the LS-AMS system using both laboratory and field measurements. The capability of the LS-AMS system to measure ambient aerosol density is demonstrated with sample results obtained during the Northeast Air Quality Study (NEAQS) in the summer of 2004.

3.3 THEORETICAL BASIS FOR THE LS-AMS DENSITY DETERMINATION

The LS-AMS simultaneously measures the vacuum aerodynamic diameter (d_{va}) and the optical diameter (d_o) of the particles. To connect d_{va} and d_o to the calculation of particle density, the volume equivalent diameter (d_{ve}) must be introduced. The volume equivalent diameter is defined as the diameter that the particle would have if it were formed into a sphere while preserving its internal voids. Following the methodology and assumptions discussed in *DeCarlo et al.*, (2004), the particle density (ρ_p) is expressed as a function of the particle shape (χ) , d_{va} , and d_{ve} as:

$$\rho_p = (d_{va}/d_{ve}) \cdot \rho_0 \cdot \chi_v \tag{3-1}$$

Here ρ_0 is unit density (1.0 g/cm³), and χ_v is the dynamic shape factor in the freemolecular regime. For spherical particles, $\chi_v = 1$ and the d_{ve} is equal to the physical diameter of the particle (d_p). Equation 3-1 then simplifies to

$$\rho_p = (d_{va}/d_p) \cdot \rho_0. \tag{3-2}$$

For non-spherical particles of unknown χ , the effective density (ρ_{eff}) is obtained via equation 3-3.

$$\rho_{eff} = (d_{va}/d_m) \cdot \rho_0 \tag{3-3}$$

This formula is similar to equation 3-2, with the exception that the mobility diameter (d_m) is now used as an approximation for the physical diameter of the particle. The effective density in equation 3-3 is a function of the particle density, shape factor, and size (*DeCarlo et al.*, 2004).

In the LS-AMS the optical diameter (d_o) of the particle is obtained from the optical scattering signal produced by particles of known size and composition. This optical

diameter serves as a surrogate for the physical diameter (d_p) of the particle. The resulting single particle density measurement made by the LS-AMS (denoted ρ_{LS}) is obtained from equation 3-4,

$$\rho_{LS} = (d_{va}/d_o) \cdot \rho_0. \tag{3-4}$$

One of the aims of the laboratory characterization of the LS-AMS is to demonstrate that ρ_{LS} is a reasonable measure of ρ_p for spherical non-absorbing particles.

For a given wavelength, the magnitude of scattered light from a particle is a function of the physical diameter of the particle (d_p) , its complex refractive index (m), and its shape. As will be shown, by measuring the scattered light from a wide range of aerosols of known size, shape, and refractive index a single calibration curve valid for atmospherically relevant aerosols is obtained. Since ρ_{LS} is obtained on a per particle basis, the LS-AMS has the potential to determine the mixing state of a given aerosol distribution. That is, if the aerosol distribution is composed of an external mixture of particles with two distinct densities, the LS-AMS will display a bi-modal single particle density (ρ_{LS}) distribution.

Since the light scattering module is integrated into the framework of the AMS operating platform, the quantitative non-refractory chemical composition of the sampled aerosol particles is simultaneously measured with the ρ_{LS} . Particle density can therefore be calculated from the measured mass concentrations (m_i) and bulk densities (ρ_i) for each of the major chemical components. The density based on the chemical composition is denoted ρ_{cc} and is expressed as

$$\rho_{cc} = \Sigma \left(m_i / (m_i / \rho_i) \right). \tag{3-5}$$

We note that the AMS directly measures the non-refractory chemical composition of the sampled aerosol particles. The AMS is not able to directly measure refractory components. Therefore, in the case of particles that contain a significant refractory content, ρ_{cc} from the AMS measurement will differ from ρ_p . A comparison of ρ_{cc} to ρ_{LS} may provide an estimate of the amount of refractory material in the aerosol particles.

In addition to average mass concentrations, the LS-AMS also measures correlated chemical ion signals on a particle-by-particle basis. Using instrument conversion factors for ionization efficiency and species specific m/z fragmentation patterns, the chemically measured mass of a given species is obtained on a single particle basis. With the quadrupole mass spectrometer because the time required to obtain a full mass spectrum scan, only one m/z ion signal component is obtained for each single particle sampled. However, complete single particle mass spectra are obtained with an AMS that utilizes time-of-flight mass spectrometry (ToF-AMS) (*Drewnick et al.*, 2005, *Cross et al.*, 2008). In the current experiment, the quadrupole version of the AMS was used. In Chapter 4, we present laboratory and field results obtained with a ToF-AMS equipped with a light scattering module. In that application, the light scattering module enables the use of the AMS as a true single particle mass spectrometer.

In summary, the LS-AMS provides correlated R_{LS} , d_{va} , and a chemical ion signal for each sampled particle Assuming that the particle is spherical and non-absorbing, d_o is obtained from R_{LS} via calibrations, ρ_{LS} is calculated using equation 3-4, and the total particle mass can be estimated from d_{va} and ρ_{LS} via equation 3-6.

$$m_{total} = \pi/6 d_{va}^{3}/\rho_{LS}^{2}.$$
 (3-6)

The ratio of the measured mass for a specific chemical ion signal to the derived total particle mass (via equation 3-6) yields a real-time, single particle estimate of the mass fraction of each measured chemical component. Because the quadrupole can measure only a single m/z per particle event, single particle mass fractions must be averaged to obtain an estimate of the full chemical composition of the single particles.

3.4 EXPERIMENTAL

3.4.1 Production of Characterized Aerosol Particles

The objective of the laboratory experiments is to obtain a relationship between the optical scattering signal and the physical diameter of the particles and demonstrate that ρ_{LS} (as shown in equation 3-4) is a reasonable approximation of ρ_p for ambient aerosol particles. Toward that end, particles of known size, shape, and composition (refractive index) were generated. A schematic of the instruments used to produce and characterize the aerosol particles is shown in Figure 3-1. Aerosol particles were generated from materials covering a range of properties relevant to the ambient atmosphere. Aerosols of oleic acid, NH₄NO₃, polystyrene latex spheres, fomblin pump oil, and a series of refractive index oils (Cargille Laboratory) were produced with an atomizer. Each polydisperse size distribution was size-selected with DMA I, which provided a monodisperse distributions of known d_m . Particles were then sampled with the SMPS and LS-AMS instruments. The purpose of the SMPS was to confirm the mode of the d_m size distribution (recall that for spherical particles $d_m = d_p$). The LS-AMS simultaneously measures the vacuum aerodynamic diameter (d_{va}), scattered light intensity (R_{LS}), and

chemical ion signal intensity of the sampled particles. Single particle properties, including R_{LS} , d_o , ρ_{LS} , and chemical ion signal intensity, are binned according to the particle d_{va} . The average and standard deviation of each single particle property is determined for each d_{va} size bin.



Figure 3-1. Laboratory apparatus for aerosol generation and characterization.

3.4.2 Instrumentation

3.4.2.1 AMS Apparatus

The LS-AMS instrument was introduced in section 2.2.1 and shown in Figure 2-1. Here we provide a brief overview of the instrumentation used in the laboratory characterization studies. The AMS consists of three main sections: (1) aerodynamic inlet, (2) time of flight region and (3) particle vaporizer and mass spectrometer. Particles enter the AMS through a 100 μ m orifice and pass through a series of aerodynamic lenses. In their passage through the inlet, particles are accelerated by the pressure drops and are focused into a narrow beam that passes through the time of flight region of the instrument. The particles then impact a heated surface where the non-refractory components of the particle are vaporized at T ~ 600°C. The non-refractory chemical composition is measured by ionizing the vapor plume via electron impact, and characterizing the chemical constituents with a quadrupole mass spectrometer. The detection process has sufficient sensitivity and time response to detect single particle vaporization events occurring on a ~100 μ s time scale which is fast compared to the particle time-of-flight (approximately 5 ms). The aerosol mass loadings (μ g/m³) for identified chemical species are obtained by summing the ion signals in the mass spectrum and using instrument calibrations of the ionization and collection efficiencies for each species.

3.4.2.2 Light Scattering Module

The principle components of the light scattering module were shown in Figure 2-3. The module is comprised of five principle components: a diode pumped 405 nm continuous wave 50 mW laser (CrystaLaser, LC BCL-050-405), external mirrors for alignment of the light beam, an ellipsoidal mirror for scattered light collection (Opti-Forms E103-2-01), a razor blade beam stop for quenching the throughput laser light, and a photomultiplier tube (PMT) for light detection (Hamamatsu H6779-00). The spurious scattered light is reduced by a series of apertures along the laser beam (x) axis identified in Figure 2-3. The laser beam axis is oriented perpendicular to the particle beam axis (zaxis) and the intersection point between the laser and particle beams is centered at one focal point of the ellipsoidal mirror, while the active surface of the PMT is mounted at the second focal point. A 15 k Ω resistor terminates the output of the PMT, and the output pulses are transmitted to the computer via an ADC board (National Instruments).

The main difference between the optical detection method used in the LS-AMS system and optical sizing techniques previously employed (*Murphy et al.*, 2004; *Salt et al.*, 1996; *Dutcher* 2004; *Moffet et al.*, 2005) is in the diameter of the laser beam. In the LS-AMS, the laser beam is diverging at the intersection with the particle beam whereas in other cited systems the laser beam is tightly focused. With a broad laser beam (~2.7 mm in diameter along the y axis) all particles that impact the vaporizer first pass through the laser beam. Therefore, the LS-AMS, via the optical scattering signals, detects all particles that impact the surface of the surface of the vaporizer if they are larger than the optical size detection limit ($d_p \ge 180$ nm).

3.4.3 LS-AMS as a Potential Collection Efficiency Diagnostic

As previously mentioned, the fact that all particles striking the vaporizer are optically detected allows one to determine the fraction of particles that do not produce a measurable single particle signal in the mass spectrometer such as refractory particles (elemental carbon or minerals) or other particles that bounce without complete vaporization and subsequent detection. Therefore, the collection efficiency ($d_p \ge 180$ nm) of the AMS can be measured directly with the light scattering probe. In addition to particle counting, the broad laser beam also provides a more uniform light intensity distribution across the area sampled by the particle beam. Therefore, the scattered light signals are less sensitive to the width of the particle beam formed by the aerodynamic inlet as compared to systems using tightly focused laser beams such as the ATOFMS.

3.4.4 Time-of-flight Measurement

The vacuum aerodynamic diameter of the particles (d_{va}) is determined from the particle velocity attained at the exit of the aerodynamic inlet (*Jayne et al.*, 2000; *DeCarlo et al.*, 2004). To determine this velocity, the start time (t_0) of the particle time-of-flight is measured by passing the particle beam through a spinning chopper wheel. Because the distances between the chopper wheel and the optical scattering unit and vaporizer are known (as indicated in Figure 2-1), the particle velocity can be obtained from any one of three possible time-of-flight intervals: (1) chopper to scattered light pulse, (2) chopper to chemical ion pulse or (3) scattered light pulse to chemical ion pulse.

Measuring the time-of-flight via option 1 (i.e. chopper to light scattering pulse) allows velocity, R_{LS} , and ρ_{LS} determination for all particles including those that do not yield a mass spectrometer signal. Option 2 is the standard AMS particle detection method. The time-of-flight measurement via option 3 (i.e. scattered light pulse to chemical ion pulse) eliminates the uncertainty introduced by the chopper width making it the most accurate.

3.5 UNCERTAINTY IN THE LS-AMS DENSITY MEASUREMENT

The single particle density (ρ_{LS}) determination is obtained via two measured parameters the particle time-of-flight (yielding d_{va}) and the intensity of light scattered by the particle (yielding d_o) (See equation 3-4). The accuracy of the particle density determination depends on the accuracy of these two measured parameters. One must also consider the influence of the underlying assumptions of the LS-AMS method when assessing the accuracy of the single particle density determination (i.e. that the refractive index is known and constant and that the particles are spherical).

3.5.1 Accuracy of time-of-flight determination

The accuracy of the time-of-flight measurement, yielding the particle d_{va} , depends on how accurately the start time (t_0) and arrival time (t_f) are measured per particle.

3.5.1.1 Determination of t_0

When t_0 is set by the opening of the chopper wheel (options 1 and 2 above), the uncertainty in time of flight is dominated by the chopper slit width. In this case, it is assumed that the particle passes through the chopper slit when the opening is centered along the axis of the particle path. However, particles can pass through the slit at either extreme of the slit position. The resulting maximum uncertainty in the measurement of t_0 is the half-time ($\Delta t/2$) of the slit opening. Under standard operating conditions (2% chopper slit width, spinning at 130 Hz) the maximum uncertainty in t_0 is approximately \pm 80 µs. Since the calibration between particle velocity and vacuum aerodynamic diameter is non-linear, the effect of the t_0 uncertainty on particle d_{va} varies with particle size.

Alternately, when t_0 is set with the scattered light pulse (option 3), the uncertainty in t_0 is due to the width of the laser beam and the uncertainty in the position of the particle as it crosses the laser beam. In this case, the uncertainty in t_0 is shown to be ± 2 µs.

3.5.1.2 Determination of t_f

In the conventional operation of the AMS, the arrival time (t_f) is measured by the timing of the ion pulse obtained from the mass spectrometer (options 2 and 3 discussed above). Uncertainty in t_{f} is due to the vaporization time of the particle at the vaporizer surface and the transit time of the ions through the quadrupole. In the conventional operation of the AMS (without the light scattering module), the sum of these two time intervals is included in the instrument velocity calibration by performing measurements with polystyrene latex spheres (PSLs) of known diameters. However, the vaporization time of a specific aerosol particle depends on the aerosol composition and the vaporizer temperature. Further, in the calibration with the PSL spheres the ion-transit time through the quadrupole was taken to be that of a m/z = 104 ion which is a large signal peak in the PSL mass spectrum. However, since all singly charged ions have approximately the same kinetic energy (~ 14 eV) in the quadrupole, the resulting ion transit time is proportional to the square root of the mass to charge ratio of the ion sampled (Zhang et al., 2005). Therefore, for a given aerosol particle, the uncertainty in the determination of t_f and particle d_{va} depends on the difference between the vaporization and ion transit time of the sampled particle and that of the PSL particle.

Using the LS-AMS, this uncertainty in t_f can be eliminated because the sum of the vaporization and ion-transit time for each particle type, and ion sampled, can be determined directly. This is done by measuring the particle velocity using the scattered light pulse and calculating, from the known geometry, the arrival time of the particle at the vaporizer. The difference between the time of the observed ion pulse and calculated arrival time at the vaporizer is the sum of the vaporization time and ion-transit time of the sampled aerosol particle.

Experimentally, the procedure for determining the vaporization ion-transit time is performed as follows. For each m/z sampled, the particle time-of-flight measured between the chopper and the light scattering pulse (option 1) is plotted as a function of the particle time-of-flight measured between the chopper and the chemical ion pulse (option 2). It can be shown that a linear fit to these points, measured for a range of particle sizes, has a slope equal to the ratio of the flight path distances and an intercept proportional to the vaporization ion-transit time. This procedure assumes that there is no size dependence to the vaporization time of the particles. In reality, small particles will tend to vaporize more rapidly than large particles of the same composition and sampled m/z. The changing vaporization time as a function of particle size results in a measured uncertainty in the vaporization ion-transit time (intercept) and t_f determination of at most $\pm 20 \ \mu s$.

3.5.2 Overall Uncertainty in Particle Time-of-Flight and dva

In Figure 3-2 we show the uncertainty in the d_{va} measurement as a function of d_{va} for two methods of determining particle time-of-flight using the LS-AMS. For option 1 the uncertainty for a particle with a $d_{va} = 200$ nm is ~ 13% and for a 600 nm particle it is ~ 6%. With option 3 the uncertainty decreases from ~ 6 to ~ 2.5% over the same size range.



Figure 3-2. Percent difference in the particle d_{va} as a function of d_{va} for two different time-of-flight determinations.

3.5.3 Uncertainty in Particle Size Determination Using Scattered Light Intensity

In the LS-AMS the particle optical diameter (d_o) is determined from the magnitude of the calibrated scattered light intensity. Because the laser beam intensity profile is nearly Gaussian, the amount of scattered light (R_{LS}) for particles of the same size depends on the particle trajectory through the laser beam. To quantify this effect, a particle beam width probe (described previously in *Jayne et al.*, 2000 and *Huffman et al.*, 2005) was used to measure the divergence of the particle beam (i.e. the range of particle trajectories) within the AMS time-of-flight chamber. The profile of the particle beam is determined by translating a thin wire across the face of the vaporizer and measuring the

percent attenuation of the mass signal as a function of wire position. Similarly, the intensity profile of the laser beam is measured by translating a tightly focused monodisperse distribution of ammonium nitrate particles across the vertical profile of the laser beam. The change in scattered light intensity as a function of particle position provides a measure of the laser beam width. Two lasers with different beam widths were used in these experiments (shown in Appendix 3A, Figure 3A-1); one with a 1σ effective detection width (σ_{laser}) of ~ 0.79 mm (referred to as laser A), the other with a σ_{laser} ~ 1.13 mm (referred to as laser B). If the diameters of the laser beam and particle beam are known, the standard deviation in the scattered light intensity for a particle of a given vacuum aerodynamic diameter (d_{va}) can be estimated. For the LS-AMS, the standard deviations are measured directly by binning the data according to d_{va} and fitting each R_{LS} distribution to a Gaussian. The reported deviation of R_{LS} is the 1σ width of the Gaussian fit. As shown in Appendix 3A, for a well focused particle beam, the measured standard deviation in scattered light signal intensities (σ_{LS}) is approximately 18% with laser A, and approximately 10% with laser B.

3.5.4 Uncertainties Due to Assumptions

The description of the LS-AMS single particle density measurements has thus far focused on spherical, non-absorbing aerosol particles. Given that ambient aerosol particles may be non-spherical and may have significant absorption components to their refractive index, it is important to comment on how such properties would influence the LS-AMS density measurement.

3.5.4.1 Non-spherical particles

For non-spherical particles the LS-AMS density measurement is an effective density. Particle shape will influence the amount of scattered light collected by the LS-AMS in two ways. First, the shape of the particle will influence the angular distribution of the scattering and thus the recorded scattered light intensity. Second, non-spherical particles are not as well focused by the aerodynamic lenses and will sample a greater cross section of the laser beam. For the divergent particles, R_{LS} tails to smaller signals for particles passing through the edges of the laser beam causing d_o to be underestimated on average and the effective density to be overestimated due to the form of equation 3-4. For slightly aspherical particles (e.g. pure solid ammonium sulfate particles), the latter effect dominates the uncertainty in the LS-AMS density measurements.

3.5.4.2 Absorbing Aerosol Particles

Refractive index is expressed as a complex number where the real component corresponds to scattering and imaginary component corresponds to absorption. Particles such as soot, that have a significant imaginary component to their refractive index, will absorb light in addition to scattering. Absorption will likely decrease single particle scattering (R_{LS}) causing an underestimation of d_o and overestimation of effective density in the LS-AMS. A systematic study of the effects of particle absorption is outside the scope of the current chapter.

Non-spherical and absorbing particles, such as fractal-like soot particles, have not yet been fully characterized by the LS-AMS in the current experiments; however, fractal soot particles have a low effective density causing them to be measured in the AMS in a distinct and separate d_{va} mode from typical accumulation mode aerosol (*Canagaratna et al.*, 2004). These types of non-spherical and absorbing particles were not observed by the AMS during the Chebogue Point measurements examined later in this chapter and the observed black carbon content was measured to be less than 2% of the particulate matter during the field study.

3.6 LABORATORY CHARACTERIZATION - RESULTS AND DISCUSSION 3.6.1 Single particle scattered light pulse

Figure 3-3 shows a scattered light pulse obtained from an oleic acid particle of d_m = 322 nm. In this case, the particle velocity is measured to be $v_p = 103$ m/s. The scattered light intensity (R_{LS}) is obtained by integrating the area under the pulse and normalizing it with respect to the particle velocity ($R_{LS} = R_{LS} * v_p / v_0$, where $v_0 = 1.0$ m/s to provide dimensional consistency). Because the particle size is negligible compared to the laser beam width, the width of the scattered light pulse is the width of the laser beam divided by the particle speed. The 1σ full width of a Gaussian fit to the scattered light pulse shown in the Figure is $\Delta t \sim 20 \ \mu$ s. This pulse width yields a laser beam width (1σ) of $\sim 2 \ mm$ which is within 10% of the manufacturer's specification and provides sufficient coverage of the downstream vaporizer (3.6 mm) to ensure 100% detection of particles that strike the vaporizer.



Figure 3-3. Scattered light pulse for an oleic acid particle of $d_m = 322$ nm.

3.6.2 Measurement of Vacuum Aerodynamic Diameter (dva)

The measured d_{va} distribution for a monodisperse distribution of oleic acid particles with $d_m = 322$ nm +/- 30 nm is shown in Figure 3-4. The vertical axis is the $dN/dLog(d_{va})$ number distribution of the measured particles where N is equal to the particle number concentration (particles/cm³) and $dLog(d_{va})$ is the difference between the log of each subsequent d_{va} bin. The d_{va} bin size is set such that $dLog(d_{va})$ is constant. The setting of $dLog(d_{va})$ depends on the instrument chopper slit width, which is the principle determinant of the d_{va} resolution. For the LS-AMS used in the current experiments, 50 d_{va} bins/decade were used. With this formalism, the area under each curve in Figure 3-4 is the total number concentration of particles within that distribution. The broken line shows the d_{va} distribution that results from defining t_0 with a 2% chopper slit width (option 1). The solid line shows the d_{va} distribution defining t_0 with the scattered light pulse (option 3). In the former case, the width (1σ) of the d_{va} distribution is 46 nm. This width is reduced to 24 nm in the latter case closely matching the anticipated distribution width transmitted by the DMA.



Figure 3-4. Measured number distributions as a function of particle d_{va} for a monodisperse distribution of oleic acid particles at $d_m = 322 \text{ nm} +/-30 \text{ nm}$. The dashed line is the distribution with t_0 determined with a 2% chopper slit width. The solid line is the distribution with t_0 determined with the scattered light pulse.

3.6.3 Measurement of Scattered Light Intensity (RLS)

Each d_{va} bin contains two sets of data; the total number of particles at the designated d_{va} and the intensity of the scattered light (R_{LS}) for each of those particles.

Fluctuations in the scattered light intensities within each d_{va} bin (i.e. the standard deviation of R_{LS} , denoted σ_{LS}) are due to two factors: (1) Chopper broadening (i.e. the particle d_{va} may be incorrectly designated and therefore the corresponding R_{LS} value may be stored in the wrong d_{va} bin) or (2) variations in the particle trajectory through the laser beam intensity profile. For example, when two particles having the same d_{va} pass through different light intensity regions of the laser beam, the measured R_{LS} values will be different. In this section, the reductions in σ_{LS} that result from (a) setting t_0 with the scattered light pulse (option 3) (i.e. removing the chopper uncertainty) and (b) using a wider laser beam intensity profile are demonstrated.

Figure 3-5 plots R_{LS} as a function of measured d_{va} for the same monodisperse oleic acid particles shown in Figure 3-6 (i.e. nominal $d_m = 322 \pm 30$ nm). For the peak d_{va} bin at 295 nm, σ_{LS}/R_{LS} is 24 % (see vertical error bars in the Figure). In this data set t_0 was determined by the scattered light pulse (option 3). As is evident in Figure 3-6, when t_0 is set with the 2% chopper slit width (option 1), the d_{va} distribution is broadened by the uncertainty in the determination of t_0 . In the latter case, σ_{LS}/R_{LS} is ~ 46%.



Figure 3-5. Experimental response of the LS-AMS for oleic acid monodisperse size distribution $d_m = 322$ nm compared with the calculated response using Mie theory.

The d_p corresponding to each d_{va} can be obtained via rearrangement of equation 3-2 ($d_p = d_{va}/\rho_p \cdot \rho_0$) because the density and shape of the oleic acid particles are known. Given that the particles are spherical ($d_m = d_p$) and the refractive index is known (n =1.46), the theoretical scattering response of the system can be calculated via Mie theory as discussed in Appendix 3B. The right hand axis (R_{MIE}) in Figure 3-5 refers to the solid line and is the relative intensity of scattered light predicted by Mie theory. The amplitude of the Mie scattering is defined as the ratio of the intensity of scattered light across the experimentally determined angles (I_{θ}) to the intensity of the incident light (I_{0}) ($R_{MIE} = I_{\theta}/I_{0}$). R_{MIE} depends upon the wavelength of the laser used (in this case, $\lambda = 405$ nm). Since λ is constant for these experiments, the change in calculated scattered light intensity (R_{MIE}) should be of the same order as the change in measured scattered light intensity (R_{LS}) across the same particle size (d_p) range. In Figure 3-5, the change in R_{LS} closely matches the change in R_{MIE} indicating that the experimental measurements are in good agreement with the Mie theory for the sampled oleic acid particles and our determined light collection angles (set by the ellipsoidal mirror geometry).

Two different laser beams were used to demonstrate the effect of the laser beam profile on σ_{LS} as discussed in Appendix 3C. For the results shown in Figure 3-5 and discussed above ($\sigma_{LS}/R_{LS} = 24\%$) the effective detection width of the laser beam was $\sigma_{laser} \sim 0.79$ mm. With a wider laser beam ($\sigma_{laser} \sim 1.13$ mm) σ_{LS}/R_{LS} is approximately 10% for the same sampled particles. The wider laser beam ($\sigma_{laser} \sim 1.13$ mm) was used for all the laboratory results presented in the following sections.

3.6.4 Correlation Between R_{LS} and d_p

Particle density can be determined from the simultaneous measurement of d_{va} and d_p via equation 3-2, assuming that the particles are spherical. The LS-AMS instrument yields d_{va} from a direct measurement of the particle time-of-flight. Here we provide a relationship between the optical diameter (d_o), measured via the optical response (R_{LS}) of the LS-AMS, and the physical particle diameter (d_p) for spherical particles.

We begin by illustrating that there is a unique and predictable relationship between the scattered light signal (R_{LS}) and the physical particle diameter (d_p). As an example, Figure 3-6 plots R_{LS} as a function of mobility diameter (measured by the SMPS) obtained with oil particles of refractive index n = 1.53 (recall that $d_m = d_p$ for spherical particles). Measurements were performed with particles of eight distinct d_p values. The accuracy of the d_p values is set by the bin width of the SMPS-selected size. For 200 nm particles it is +/- 4 nm; for 600 nm particles it is +/- 10 nm. The solid line in the Figure is the calculated Mie scattering curve as discussed in Appendix 3B. The agreement between the experimental and calculated scattering is very good. Note that the standard deviation (σ_{LS}) for the n = 1.53 refractive index oil is smaller than the σ_{LS} for the oleic acid particles displayed in Figure 3-5. This is due to the broader laser beam used in the refractive index oil experiment.



Figure 3-6. Scattered light intensity for oil particles with refractive index n = 1.53 as a function of particle physical diameter. The solid line is a calculation based on Mie theory.



Figure 3-7. Scattered light intensity for oil particles with refractive index n = 1.53 as a function of particle physical diameter for both monodisperse (solid circles) and polydisperse (open circles) distributions. The solid line is a calculation based on Mie theory.

In another set of experiments, R_{LS} was measured for a polydisperse distribution of particles composed of the same n = 1.53 oil (Figure 3-7). Here the full size range of particles was sampled by the LS-AMS. For each particle, d_{va} was measured and converted to d_p using equation 3-2 and the known particle density ($\rho_m = 0.93$ g/cm³). For particles with $d_p > 600$ nm, the dip in the scattering curve is due to resonance as predicted by the Mie theory.

Supplier	Composition	Refractive Index * λ = 404.7nm and 25C ** λ = 532 nm and 20C	Density (g/cm ³) +/- 5%
Cargille Laboratories Series AA 1.40000	Siloxane and Aliphatic / Alicyclic Hydrocarbons	1.4127*	0.930
Cargille Laboratories Series A 1.46000	Aliphatic / Alicyclic Hydrocarbons and Hydrogenated Terphenyl	1.4743*	0.832
Cargille Laboratories Series A 1.51000	Aliphatic / Alicyclic Hydrocarbons and Hydrogenated Terphenyl	1.5331*	0.910
Cargille Laboratories Series A 1.56000	Aliphatic / Alicyclic Hydrocarbons and Hydrogenated Terphenyl	1.5919*	0.987
Cargille Laboratories Series A 1.61000	Hydrogenated Terphenyl and 1- Bromonaphthalene	1.6564*	1.217
Aldrich Chemical Co.	Oleic Acid in Methanol	1.46**	0.895
Ausimont	Hexafluoro-propene (Fomblin Pump Oil)	1.30**	1.88
Bioworld	Glycerol	1.46**	1.265
Duke Scientific Co.	Polystyrene Latex Spheres in H2O	1.59**	1.045

Table 3-1. Composition, refractive index, and material density for all spherical particles studied with the LS-AMS.

For a given particle diameter, the intensity of scattered light depends on the index of refraction. To explore the possibility of using a single calibration curve to determine d_p from R_{LS} , we measured R_{LS} for a series of spherical oil particles with refractive indices ranging from 1.33 < n < 1.66 (see Table 3-1 and Figure 3-8). (Here *n* is the real or scattering portion of the complex refractive index, m = n + ik. Since all the aerosol particles studied in the present experiments have negligible absorption ($k \sim 0$), the refractive indices will be listed according to the value of *n*.)



Figure 3-8. Scattered light intensity for oil particles for index of refraction between 1.30 < n < 1.66. The dashed lines are calculations based on Mie theory. The chosen calibration curve is shown as the solid black line.

The experimental points were obtained from polydisperse distributions generated from each oil, with d_p determined from d_{va} and the known oil densities. As in the case of the n=1.53 refractive index oil, polydisperse distributions of each different compound were sampled with the LS-AMS. In each case, measured d_{va} values were converted to d_p using the known density of oil. Measured R_{LS} values for each oil are plotted as a function of d_p in Figure 3-8. The dashed lines in the figure are Mie scattering curves for each refractive index over the size range studied. The functional dependence of scattering on the particle diameter for particles with diameters larger than 600 nm is complicated by the onset of resonance patterns in the scattering curves as predicted by the Mie theory and observed in the experimental results. Therefore, a unique relationship between R_{LS} and d_p can only be obtained for particles with $d_p < 600$ nm. The size at which the onset of the resonance patterns occur will shift as a function of the laser wavelength and particle refractive index.

The solid line in Figure 3-8 is the Mie curve for n = 1.53 that closely matches the R_{LS} points obtained with the n = 1.53 oil particles. Using this curve as the single calibration to obtain d_o from R_{LS} yields the physical diameter of a particle with an unknown n (in the range 1.41 < n < 1.60) to an accuracy of about $\pm 10\%$. This range was chosen because it encompasses the range of n observed for the majority of atmospheric submicron ambient aerosol particles. (*Seinfeld and Pandis*, 2006). For the field deployment of the LS-AMS the calibration curve was constructed from ammonium nitrate particles (n = 1.55).

3.6.5 Determination of Particle Density

To determine the density of each sampled particle via equation 3-4, d_{va} is obtained from the particle time-of-flight and d_o is obtained from the calibration curve shown in Figure 3-8. Each single particle density is then stored in a d_{va} size bin – from which a distribution of single particle densities can be created. Fitting each density distribution to a Gaussian curve provides the mean and standard deviation of the measured densities for each d_{va} size bin. In Figure 3-9 we show the single particle density distribution (ρ_{LS}) obtained with particles composed of n = 1.47 oil is shown. The stated material density of the n = 1.47 oil particles was 0.83 ± 0.04 g/cm³. The mean single particle density (ρ_{LS}) measured by the LS-AMS was measured to be 0.87 ± 0.11 g/cm³. The experimentally measured density (ρ_{LS}) agrees with the known material density (ρ_m) to within 5%. Similar agreement is obtained for all particle sizes sampled. Given that ρ_{LS} is measured for each d_{va} bin, the LS-AMS provides the opportunity to explore size-dependent densities for multi-component aerosol systems.



Figure 3-9. Single particle density distribution (ρ_{LS}) for refractive index oil n = 1.47. Density obtained from the mode of a Gaussian fit these points is $0.87 \pm 0.11 \text{ g/cm}^3$



Figure 3-10. Single particle densities (ρ_{LS}) versus material density (ρ_m) for all spherical particles studied. Particles across a refractive index range 1.33 – 1.66 were tested.

In Figure 3-10, the average, experimentally determined single particle densities (ρ_{LS}) are plotted against the corresponding material densities for each particle type studied. The full range of refractive indices studied extends from 1.33 < n < 1.66 and is indicated on the plot by the relative size of the symbols and annotations. Within the sub-range of refractive index values anticipated for atmospheric aerosol particles, 1.41 < n < 1.60, ρ_{LS} agrees with the corresponding material densities to within $\pm 10\%$. As expected,

the greatest deviation of ρ_{LS} from the material densities occurs for particles with refractive indices at the edges of the studied range (i.e. n = 1.33 and n = 1.66). Here, ρ_{LS} underestimates the material density by ~ 20% for the high refractive index and overestimates the material density by ~ 30% for the low refractive index. For ambient aerosol analysis in which the refractive index is unknown, a mid-range refractive index material (such as n = 1.53) will provide the best estimate of particle size (d_p) and corresponding single particle density (ρ_{LS}).

3.6.6 Density Resolution of the LS-AMS Instrument

To illustrate the density resolution provided by the LS-AMS instrument, measurements were conducted with single component aerosol particles composed of four distinct materials: oleic acid ($\rho_m = 0.895 \text{ g/cm}^3$), calibration oil with refractive index n=1.53 ($\rho_m = 0.93 \text{ g/cm}^3$), glycerol ($\rho_m = 1.265 \text{ g/cm}^3$), and NH₄NO₃ ($\rho_m = 1.72 \text{ g/cm}^3$) (See Figure 3-11).



Figure 3-11. Scattered light intensity (R_{LS}) distributions (Upper Panel) and corresponding ρ_{LS} distributions (Lower Panel) for four known composition aerosol particles.

In the top panel of Figure 3-11 normalized histograms of R_{LS} for each particle type are shown. The R_{LS} data are obtained from a single d_{va} size bin, in this case, d_{va} = 468 nm. This size bin was selected because of good sampling statistics obtained for each type of particle. In the lower panel of Figure 3-11 we show the normalized histograms of the single particle density (ρ_{LS}) obtained from combination of the particle d_{va} and optically determined d_o measurements. These pure component density distributions indicate that the current LS-AMS instrument can resolve density differences on the order of 10%. Given that ρ_{LS} is determined on a particle-by-particle basis it is possible to determine whether an ensemble of particles is (a) externally mixed (i.e. distinct chemical compositions for different particles within the ensemble) or (b) internally mixed (i.e. each particle composed of a similar chemical composition). With a density resolution of 10% the LS-AMS instrument is capable of determining whether an ambient ensemble of sulfate ($\rho_m \sim 1.77 \text{ g/cm}^3$) and organic ($\rho_m \sim 1.2 \text{ g/cm}^3$) aerosol particles is internally or externally mixed. This feature of the LS-AMS is illustrated in the field study described in Section 3.7.

3.7 AMBIENT AEROSOL ENSEMBLE DENSITY MEASUREMENTS

3.7.1 Field Study Background

In the summer of 2004, a field study was conducted at a rural coastal site at Chebogue Point, Nova Scotia. The primary objective of the field study was the detection and analysis of pollution plumes with atmospheric residence times of a few days. The focus of this field study, preformed under the auspices of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT), was to analyze the transformations of ambient pollution plumes advected from the Northeastern coast of the US toward Europe (*Fehsenfeld et al.*, 2006). Two LS-AMS instruments were deployed during this study, one at Chebogue Point and the other on the Ronald H. Brown NOAA research vessel. In this chapter data from the Chebogue Point ground site are presented. The capability of the LS-AMS to measure the density of ambient aerosol particles is demonstrated.

As stated in Section 3.2.3, the LS-AMS provides two independent measurements of density: One based on the chemical measurement obtained with the mass spectrometer (denoted ρ_{cc}) and the other based on the physical per particle measurements of vacuum aerodynamic diameter (d_{va}) and optical diameter (d_o) (denoted ρ_{LS}). In this section, ρ_{cc} and ρ_{LS} are compared and the effect of the assumptions regarding bulk densities, refractive index, and particle beam broadening are discussed. The use of correlated single particle chemical ion signal intensities to determine average single particle mass fractions is also discussed.

3.7.2 Ambient Aerosol Particle Density Determination



Figure 3-12. Lower panel: Average mass concentrations of the major chemical species measured with the LS-AMS at Chebogue Point, Nova Scotia. Upper Panel: Densities determined from average chemical composition (ρ_{cc}) (shown as the black line) and densities determined from the average single particle optical scattering (ρ_{LS}) (shown as the grey line).

In the lower panel of Figure 3-12 we show the mass spectrometric measurements for aerosol particles sampled during the continuous five-week period at the Chebogue Point ground site. This panel of the figure presents the mass concentrations in $\mu g/m^3$ for the major chemical species as measured by the calibrated AMS. The measured components are SO₄, NO₃, NH₄ and compounds identified as organics. Each chemical species is identified via the method outlined in the experimental section and described in detail by Jayne et al., (2000) and Allan et al., (2003). The black carbon concentrations were obtained separately with a Multi-Angle Absorption Photometer (MAAP) instrument and the concentration of black carbon was low (< 2% total mass) throughout the measurement period. It has recently been shown that significant (\sim 75%) water loss occurs via evaporation as particles are transmitted from ambient pressure into the low pressure region of aerosol mass spectrometers (Zelenyuk et al., 2006b, Slowik, 2006). Therefore, the density measured by the LS-AMS, does not include the full original particle water content. Likewise, the chemical composition-based density calculation does not include water.

The composition of the aerosol particles measured at Chebogue Point can be divided into two general types: (1) Particles dominated by sulfate with a significant contribution from organics and (2) Particles dominated by organic with little sulfate. The difference in the measured composition correlates with the meteorological data showing that for periods dominated by sulfate the winds were primarily southwesterly. At these times, the sampled air-mass previously passed over urban centers along the Northeastern United States an area dominated by anthropogenic emissions. During periods in which
the composition was dominated by organics, the winds were primarily from the north. The regions to the north of Chebogue Point are sparsely populated and the aerosol particles are more likely influenced by biogenic emissions.

Average densities (both ρ_{cc} and ρ_{LS}) of the ambient particles were calculated every 30 minutes. The average density time series are displayed in the upper panel of Figure 3-12. The values of ρ_{cc} were obtained from the average measured mass fraction of each species assuming average bulk densities for each component of $\rho_{organic} = 1.27$ g/cm³, and $\rho_{SO4, NO3, NH4, BC} = 1.77$ g/cm³ (See equation 3-5). The average values of ρ_{LS} were obtained from the mode of the Gaussian fit to the single particle density distribution as discussed earlier (see for example Figure 3-9).



Figure 3-13. Correlation between the average values of ρ_{cc} and ρ_{LS} measured for the 5 week period of ambient aerosol particle sampling at Chebogue Point.

The densities in Figure 3-12 are re-plotted in Figure 3-13 to show more clearly the correlation between ρ_{cc} and ρ_{LS} . The dashed line is the 1:1 line. The linear fit to the data points, forced through the origin, results in a slope of nearly one and R² value of 0.88. For clarity of presentation, a representative error bar is shown for one average point only. The error bar is the standard deviation of the average ρ_{LS} measurements within a single ρ_{cc} bin. Across the measured range of densities this error is approximately $\pm 3.5\%$. This uncertainty is consistent with the uncertainty in the time-of-flight measurement (and subsequently particle d_{va}) that results from defining t_0 with the spinning chopper wheel

(option 1 described earlier). Option 1 was chosen for the d_{va} determination of the ambient particles because it allowed density determination for every optically detected particle, independent of the correlated chemical ion signal. For the particle size range sampled at Chebogue Point ($d_{va} > 450$ nm), the maximum predicted uncertainty in $d_{va} \sim 6-7\%$ (Figure 3-2). The measured 3.5% uncertainty is within these bounds. The lower density region of the plot is dominated by organics (80% mass fraction) whereas the higher density region is dominated by sulfate (70% mass fraction).

When interpreting the correlation between ρ_{cc} and ρ_{LS} , three effects must be considered: (i) the assumed bulk densities in the ρ_{cc} calculation, (ii) the refractive index of both the ambient and calibration aerosol particles, and (iii) the particle non-sphericity.

(i.) Assumed Bulk Densities. As stated earlier, bulk density values of 1.27 g/cm³ for the organic species and 1.77 g/cm³ for the inorganic and black carbon species were used in the calculation of ρ_{cc} . In the literature, 1.77 g/cm³ is often used for the bulk density of inorganic species and a value of 1.2 g/cm³ is most often used for the bulk density of organics (*Turpin and Lim*, 2001). The value of 1.2 g/cm³ was estimated from experimental measurements taken within close proximity to urban centers. The atmospheric residence time of aerosol particles sampled at Chebogue Point is on the order of days and therefore it is likely that the organic particles are more highly oxidized resulting in the somewhat higher density required here for the best correlation between optically and chemically derived particle density.

(ii.) Refractive Index. As stated earlier, $R_{LS} - d_p$ calibration curve (Figure 3-8) is constructed from a single value of refractive index. Therefore, differences in refractive index between the calibration aerosol particles and ambient aerosol particles will cause

inaccuracies in the optical sizing and subsequently calculated ρ_{LS} . The calibration species used at Chebogue Point was NH₄NO₃ with a refractive index of n = 1.55 which is nearly the same as that of the dominant ambient inorganic species ((NH₄)₂SO₄ (n = 1.53). On the other hand, the index of refraction for organic species is most likely lower 1.40 < n <1.45. The effect, if any, of a lower refractive index would be most evident in the lower density region of the correlation plot shown in Figure 3-13. No such deviation from the linear correlation is discernable in the present data set.

(iii.) Particle non-sphericity. As discussed in the Section 3.5.4, if the ambient aerosol particles sampled at Chebogue Point were non-spherical, the single particle density measurement (ρ_{LS}) would systematically overestimate ρ_p . The correlation between ρ_{LS} and ρ_{cc} shown in Figure 3-13 can be used to assess the shape of the ambient aerosol particles. If one assumes that the particles have a non-refractory chemical composition and that the assumed bulk densities are reasonable, non-spherical particles would deviate from the 1:1 line in Figure 3-13. The close fit to the 1:1 line suggests that the particles are spherical or nearly-spherical and that ρ_{LS} is here a measure of ρ_p .

3.7.3 Mixing State of the Ambient Aerosol Particles

As shown in Figure 3-11, the density resolution of the laboratory LS-AMS instrument is 10%. The instrument used in the Chebogue Point field study was an earlier version. Its density resolution was measured to be 20%. With this resolution the LS-AMS deployed at Chebogue Point could still resolve a bimodal ρ_{LS} distribution if the field-sampled aerosols are externally mixed pure organic and pure inorganic particles.

(Taking the density of the average organic component as 1.27 g/cm^3 and that of the inorganic components as 1.77 g/cm^3 ; a difference of about 30%.)



Figure 3-14. Single particle density distributions for sulfate-dominated (event A shown as the solid line) and organic-dominated (event B shown as the dashed line) ambient aerosol measured with the LS-AMS at Chebogue Point, Nova Scotia.

Figure 3-14 shows two ρ_{LS} distributions, one measured during period A (mixed sulfate-organic composition) and the other measured during period B (organic-dominated composition) shown in lower panel of Figure 3-12. The single particle density values in Figure 3-14 were obtained from particles measured within the peak d_{va} size bin of each

sampled event: For period A, $d_{va} = 513$ nm with 1318 particles sampled and for period B, $d_{va} = 468$ nm with 1665 particles sampled. Each single particle density distribution appears as a single mode indicating that the aerosol particles are internally mixed. A Gaussian fit to each density distribution yields $\rho_{LS} = 1.56 \pm 0.20$ g cm⁻³ for period A and $\rho_{LS} = 1.32 \pm 0.20$ g cm⁻³ for period B.

It is expected that the ambient particles sampled at Chebogue Point would be internally mixed due to the long residence time and atmospheric processing of the particles. Analyzing the shapes of the single particle density distributions from the other time periods shown in Figure 3-12 is likewise consistent with particles being internally mixed.

3.7.4 Consistency Check of pLS via Average Single Particle Composition

In Figure 3-13 the chemical composition-based density (ρ_{cc}) was obtained from the average mass loadings of each chemical component. These mass loadings were measured by scanning the quadrupole mass spectrometer over the full range of m/z values (i.e. 10 - 300 amu). This is an ensemble average measurement.

A direct measurement of the single particle complete chemical composition is not possible with the quadrupole mass spectrometer because of the time required to complete a m/z scan over the full mass range. However, single particle chemical ion signal intensities for individual m/z values are obtained with the quadrupole mass spectrometer when measuring the particle time-of-flight. Within this operational mode, for each chemical ion pulse observed, ρ_{LS} is also calculated. Using equation 3-6, single particle mass fractions are calculated for each of the major chemical species SO₄, NO₃, NH₄, and the organic components. For example, from the chemical ion pulses detected at m/z = 64 (SO₂⁺), the single particle mass fraction of sulfate can be calculated. Averaging over a sufficient number of particle events such that each major species corresponding m/z is sampled provides an average chemical composition via single particle detection. Average single particle compositions were obtained in this way for the ambient aerosol particles sampled during period A. Within experimental uncertainty, mass balance was achieved by adding each of the chemical component mass fractions. The average single particle chemical composition via single particles single within experimental error of the corresponding ρ_{LS} value.

The next generation of the light scattering – AMS systems that use time-of-flight mass spectrometry (ToF-AMS) allow the analysis of single particle mass spectra coupled to ρ_{LS} . The characterization and application of this next generation instrument is described in Chapter 4, with results from Mexico City, Mexico.

3.8 SUMMARY

A light scattering module was integrated into a quadrupole AMS instrument. This module provides the simultaneous measurement of d_{va} and scattered light intensity (R_{LS}) for all particles sampled by the AMS above ~180 nm mobility diameter. A single calibration curve converts the R_{LS} to an optical diameter (d_o) which when combined with the particle d_{va} provides a real-time single particle measurement of the particle density (ρ_{LS}) for spherical, non-absorbing aerosol particles. The laboratory characterization of LS-AMS shows that a single calibration curve yields the material density of spherical particles with refractive indices over a range from 1.41 < n < 1.60 with an accuracy of about \pm 10%. The density resolution of the current LS-AMS system has been shown to be 10% indicating that externally mixed inorganic/organic aerosol distributions can be resolved. Highly processed ambient aerosol particles analyzed with the LS-AMS show a strong correlation between the chemically-derived (ρ_{cc}) and physically-derived (ρ_{LS}) density values. Density inferred from the average single particle chemical composition is consistent with the optically determined single particle density (ρ_{LS}).

Appendix 3A. Effect of Laser and Particle Beam Profiles on LS-AMS Optical Response

Here we examine the effect of laser beam width and particle beam profile on the magnitude (R_{LS}) and standard deviation (σ_{LS}) of the light scattered by the particles. For these experiments we used a tightly focused 350 nm monodipserse NH₄NO₃ particle beam to probe the scattering profile. The profile of the NH₄NO₃ particle beam is shown in Figure 3A-1 as the shaded curve. This profile was measured with the beam width probe as described in the text. As shown by Jayne et al., (2000) and more recently Huffman et al., (2005) the particle beam profile is well approximated by a one dimensional Gaussian distribution, in this case with a σ_1 of 0.17 mm. This width is defined as the spatial width that encompasses 68% of the total area under the curve. The two laser beams in this study had $1/e^2$ widths of ~ 2.4 mm (laser A) and ~ 2.7 mm (laser B).



Figure 3A-1. Two laser beam intensity profiles measured by translating a 350 nm beam of NH_4NO_3 particles across the vertical (Y) axis of the laser and measuring the scattering signal as a function of particle position. The shaded distribution illustrates the calculated width of a 350 nm NH_4NO_3 particle beam based on results from the beam width probe.

Figure 3A-1 shows the scattered light intensities (R_{LS}) produced by translating the tightly focused beam of NH₄NO₃ particles across the width of each laser beam. To quantify the effective detection width of each laser beam, each series of R_{LS} values were fit to a one-dimensional Gaussian curve as shown in Figure 3A-1. The 1σ width (σ_{laser}) of R_{LS} obtained with laser A (grey line in the Figure) was $\sigma_{laser} \sim 0.79$ mm while the 1σ width obtained with laser B (black line in the Figure) was $\sigma_{laser} \sim 1.13$ mm.

Via the scattering curves shown in Figure 3A-1 one can quantify the effect on the magnitude of R_{LS} of different particle trajectories through the laser. For example, with laser A the measured R_{LS} value decreases by approximately 50% when a particle

trajectory is ~ 0.5 mm away from the center of laser. For laser B, R_{LS} decreases by only 27% for a particle with the same trajectory. With the tightly focused NH₄NO₃ particles aligned through the centers of lasers A and B, the standard deviation in scattered light intensities (σ_{LS}) is 18% for the narrower laser beam (A) and 11% for the wider laser beam (B) (see the vertical error bars in Figure 3A-1). The reduction in the standard deviation of signals for the wider laser beam (B) is a consequence of fewer particles passing through less intense regions of laser light.

Appendix 3B. Comparison of the Experimental Response of LS-AMS to Mie Theory

To validate the response of the LS-AMS to particles composed of oils of varying refractive indices experimental data were compared to the theoretical response of the system calculated from Mie theory. To model the Mie scattering within the LS-AMS, we follow the method of Moffet et al., (2005). In accord with their formalism, the optical scattering response for a spherical particle in the LS-AMS is given by,

$$R_{MIE} = 1/k^2 \int \int (|S_1|^2 \sin^2 \varphi + |S_2|^2 \cos^2 \varphi) \sin\theta \, d\theta \, d\varphi.$$
(3B-1)

Here k is the wavenumber, S_1 and S_2 are the scattering amplitude matrix elements for polarized and unpolarized light respectively, φ is the azimuth angle from the plane of polarization, and θ is the polar angle. The matrix elements are dependent on the refractive index (m = n + ik), particle size (d_p), wavelength of light (λ), and θ . For spherical particles, S_1 and S_2 are independent of φ , and for the oils used in this experiment the imaginary or absorption (k) component to the refractive index is negligibly small compared to the value of the real or scattering component (n). The scattering amplitude matrix elements for each of the experimental conditions were obtained with a PC interface for the classic BHMIE (*Bohren and Huffman*, 1983) algorithm for calculating the Mie scattering from spheres called MiePlot v3.4.10 (<u>www.philiplaven.com</u>).

In accord with the formalism of Moffet et al., (2005), an axisymmetric response (R_{AS}) , specific to the LS-AMS collection geometry, was calculated. The axisymmetric response corrects R_{MIE} for scattered light lost through the laser beam entrance and exit holes (10 mm in diameter) in the ellipsoid. To account for the position of these holes the integration limits of θ in equation a.4 are taken to be 12.6° and 167.4°. Since φ ranges from 0° - 360°, an additional correction must be made to take into account the amount of off-axis (R_{OA}) light not collected by the ellipsoid (see *Moffet et al.*, (2005) for details). As is evident from Figures 9 and 10, the agreement between R_{MIE} and R_{LS} are good.

3.9 REFERENCES FOR CHAPTER III

- Ananth, G. & Wilson, J.C. 1988, "Theoretical analysis of the performance of the TSI Aerodynamic Particle Sizer – the effect of density on response", *Aerosol Science and Technology*, vol. 9, no. 3, pp. 189-199.
- Baron, P.A. 2001, "Measurement of airborne fibers: A review", *Industrial health*, vol. 39, no. 2, pp. 39-50.
- Baron, P.A., Sorensen, C.M. & and Brockmann, J.E. 2001, *Aerosol Measurement: Principles, 3 Techniques, and Applications,* John Wiley, New York.
- Bohren, C.F. & and Huffman, D.R. 1983, *Absorption and Scattering of Light by Small Particles*, Wiley-Interscience, New York, NY.
- Brockmann, J.E. & Rader, D.J. 1990, "APS response to nonspherical particles and experimental determination of dynamic shape factor", *Aerosol Science and Technology*, vol. 13, no. 2, pp. 162-172.

- Canagaratna, M.R., Jayne, J.T., Ghertner, D.A., Herndon, S., Shi, Q., Jimenez, J.L., Silva, P.J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K.L., Kolb, C.E. & Worsnop, D.R. 2004, "Chase studies of particulate emissions from in-use New York City vehicles", *Aerosol Science and Technology*, vol. 38, no. 6, pp. 555-573.
- Cross, E.S., Onasch, T.B., Canagaratna, M., Jayne, J.T., Kimmel, J., Yu, X.Y., Alexander, M.L., Worsnop, D.R. & and Davidovits, P. 2008, "Single Particle Characterization Using a Light Scattering Module Coupled to a Time-of Flight Aerosol Mass Spectrometer", *Submitted to ACPD*, .
- DeCarlo, P.F., Slowik, J.G., Worsnop, D.R., Davidovits, P. & Jimenez, J.L. 2004, "Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory", *Aerosol Science and Technology*, vol. 38, no. 12, pp. 1185-1205.
- Dinar, E., Mentel, T.F. & Rudich, Y. 2006, "The density of humic acids and humic like substances (HULIS) from fresh and aged wood burning and pollution aerosol particles", *Atmospheric Chemistry and Physics*, vol. 6, pp. 5213-5224.
- Drewnick, F., Hings, S.S., DeCarlo, P., Jayne, J.T., Gonin, M., Fuhrer, K., Weimer, S., Jimenez, J.L., Demerjian, K.L., Borrmann, S. & Worsnop, D.R. 2005, "A new timeof-flight aerosol mass spectrometer (TOF-AMS) - Instrument description and first field deployment", *Aerosol Science and Technology*, vol. 39, no. 7, pp. 637-658.
- Dutcher, D.D. 2004, Optical Sizing of Particles using the Aerosol Time of Flight Mass Spectrometer A Mechanical Engineering Plan B Master's Degree Paper, University of Minnesota.
- Ehara, K.,S.Shin 1998, "Measurement of Density Distribution of Aerosol Particles by Successive Classification of Particles According to their Mass and Diameter", *Journal of Aerosol Science*, vol. 29, no. Suppl. 1, pp. 19-20.
- Fuchs, N.A. 1964, The Mechanics of Aerosols, Pergamon Press Ltd., New York.
- Geller, M., Biswas, S. & Sioutas, C. 2006, "Determination of particle effective density in urban environments with a differential mobility analyzer and aerosol particle mass analyzer", *Aerosol Science and Technology*, vol. 40, no. 9, pp. 709-723.

- Hand, J. L., S. M. Kreidenweis, N. Kreisberg, S. Hering, M. Stolzenburg, W. Dick, and P.H.McMurry 2002, "Comparisons of Aerosol Properties Measured by Impactors and Light Scattering from Individual Particles: Refractive Index, Number and Volume Concentrations, and Size Distributions", *Atmospheric Environment*, vol. 36, no. 11, pp. 1853–1861.
- Huffman, J.A., Jayne, J.T., Drewnick, F., Aiken, A.C., Onasch, T., Worsnop, D.R. & Jimenez, J.L. 2005, "Design, modeling, optimization, and experimental tests of a particle beam width probe for the aerodyne aerosol mass spectrometer", *Aerosol Science and Technology*, vol. 39, no. 12, pp. 1143-1163.
- Jayne, J.T., Leard, D.C., Zhang, X.F., Davidovits, P., Smith, K.A., Kolb, C.E. & Worsnop, D.R. 2000, "Development of an aerosol mass spectrometer for size and composition analysis of submicron particles", *Aerosol Science and Technology*, vol. 33, no. 1-2, pp. 49-70.
- Jimenez, J.L., Jayne, J.T., Shi, Q., Kolb, C.E., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., Zhang, X.F., Smith, K.A., Morris, J.W. & Davidovits, P. 2003, "Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer", *Journal of Geophysical Research-Atmospheres*, vol. 108, no. D7.
- Katrib, Y., Martin, S.T., Rudich, Y., Davidovits, P., Jayne, J.T. & Worsnop, D.R. 2005, "Density changes of aerosol particles as a result of chemical reaction", *Atmospheric Chemistry and Physics*, vol. 5, pp. 275-291.
- Kelly, W.P. & McMurry, P.H. 1992, "Measurement of particle density by inertial classification of differential mobility analyzer generated monodisperse aerosols ", *Aerosol Science and Technology*, vol. 17, no. 3, pp. 199-212.
- Khlystov, A., Stanier, C. & Pandis, S.N. 2004, "An algorithm for combining electrical mobility and aerodynamic size distributions data when measuring ambient aerosol", *Aerosol Science and Technology*, vol. 38, pp. 229-238.
- Lohmann, U.,G.Lesins 2005, "Stronger Constraints on the Anthropogenic Indirect Aerosol Effect", *Science*, vol. 298, pp. 1012-1015.
- McMurry, P.H., X. Wang, K. Park, K. Ehara 2002, "The Relationship between Mass and Mobility for Atmospheric Particles: A New Technique for Measuring Particle Density", *Aerosol Science and Technology*, vol. 36, pp. 227-238.

- Moffet, R.C. & Prather, K.A. 2005, "Extending ATOFMS measurements to include refractive index and density", *Analytical Chemistry*, vol. 77, no. 20, pp. 6535-6541.
- Murphy, D.M., Cziczo, D.J., Hudson, P.K., Schein, M.E. & Thomson, D.S. 2004, "Particle density inferred from simultaneous optical and aerodynamic diameters sorted by composition", *Journal of Aerosol Science*, vol. 35, no. 1, pp. 135-139.
- Murphy, D.M. & Thomson, D.S. 1995, "LASER IONIZATION MASS-SPECTROSCOPY OF SINGLE AEROSOL-PARTICLES", Aerosol Science and Technology, vol. 22, no. 3, pp. 237-249.
- Prather, K.A., Nordmeyer, T. & Salt, K. 1994, "Real-time characterization of individual aerosol particles using time-of-flight mass spectrometry ", *Analytical Chemistry*, vol. 66, no. 9, pp. 1403-1407.
- Ramanathan, V., Crutzen, P.J., Kiehl, J.T. & Rosenfeld, D. 2001, "Atmosphere -Aerosols, climate, and the hydrological cycle", *Science*, vol. 294, no. 5549, pp. 2119-2124.
- Salt, K., Noble, C.A. & Prather, K.A. 1996, "Aerodynamic particle sizing versus light scattering intensity measurement as methods for real time particle sizing coupled with time-of-flight mass spectrometry", *Analytical Chemistry*, vol. 68, no. 1, pp. 230-234.
- Schleicher, B., Kunzel, S. & Burtscher, H. 1995, "In-situ measurement of size and density of submicron aerosol particles", *Journal of Applied Physics*, vol. 78, no. 7, pp. 4416-4422.
- Seinfeld, J.H., S.N.Pandis 2006, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons, Inc., New York.
- Slowik, J.G. 2006, Morphology, Composition, and Atmospheric Processing of Soot Particles, Boston College.
- Slowik, J.G., Stainken, K., Davidovits, P., Williams, L.R., Jayne, J.T., Kolb, C.E., Worsnop, D.R., Rudich, Y., DeCarlo, P.F. & Jimenez, J.L. 2004, "Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 2: Application to combustion-generated soot aerosols

as a function of fuel equivalence ratio", *Aerosol Science and Technology*, vol. 38, no. 12, pp. 1206-1222.

- Sullivan, R.C. & Prather, K.A. 2005, "Recent advances in our understanding of atmospheric chemistry and climate made possible by on-line aerosol analysis instrumentation", *Analytical Chemistry*, vol. 77, no. 12, pp. 3861-3885.
- Turpin, B.J. & Lim, H.J. 2001, "Species contributions to PM2.5 mass concentrations: Revisiting common assumptions for estimating organic mass", *Aerosol Science and Technology*, vol. 35, no. 1, pp. 602-610.
- Zelenyuk, A., Cai, Y., Chieffo, L. & Imre, D. 2005, "High precision density measurements of single particles: The density of metastable phases", *Aerosol Science and Technology*, vol. 39, no. 10, pp. 972-986.
- Zelenyuk, A., Cai, Y. & Imre, D. 2006, "From agglomerates of spheres to irregularly shaped particles: Determination of dynamic shape factors from measurements of mobility and vacuum aerodynamic diameters", *Aerosol Science and Technology*, vol. 40, no. 3, pp. 197-217.
- Zelenyuk, A. & Imre, D. 2005, "Single particle laser ablation time-of-flight mass spectrometer: An introduction to SPLAT", *Aerosol Science and Technology*, vol. 39, no. 6, pp. 554-568.
- Zelenyuk, A., Imre, D. & Cuadra-Rodriguez, L.A. 2006, "Evaporation of water from particles in the aerodynamic lens inlet: An experimental study", *Analytical Chemistry*, vol. 78, no. 19, pp. 6942-6947.
- Zhang, Q., Canagaratna, M.R., Jayne, J.T., Worsnop, D.R. & Jimenez, J.L. 2005, "Timeand size-resolved chemical composition of submicron particles in Pittsburgh: Implications for aerosol sources and processes", *Journal of Geophysical Research-Atmospheres*, vol. 110, no. D7.

CHAPTER IV

SINGLE PARTICLE MEASUREMENTS DURING THE MILAGRO FIELD CAMPAIGN IN MEXICO CITY

4.1 OVERVIEW

We present the first single particle results obtained using an Aerodyne time-offlight aerosol mass spectrometer coupled with a light scattering module (LS-ToF-AMS). The instrument was deployed at the T1 ground site approximately 40 km northeast of the Mexico City Metropolitan Area (MCMA) as part of the MILAGRO field study in March of 2006. The instrument was operated as a standard AMS from March 12-30th, acquiring average chemical composition and size distributions for the ambient aerosol, and in single particle mode from March 27-30th. Over a 75-hour sampling period, 12,853 single particle mass spectra were optically triggered, saved, and analyzed. The correlated optical and chemical detection allowed detailed examination of single particle collection and quantification within the LS-ToF-AMS. The single particle data enabled the mixing states of the ambient aerosol to be characterized within the context of the size-resolved ensemble chemical information.

The particulate mixing states were examined as a function of sampling time and most of the particles were found to be internal mixtures containing many of the organic and inorganic species identified in the ensemble analysis. The single particle mass spectra were deconvolved, using techniques developed for ensemble AMS data analysis, into HOA, OOA, NH₄NO₃, (NH₄)₂SO₄, and NH₄Cl fractions. Average single particle mass and chemistry measurements are shown to be in agreement with ensemble MS and PTOF measurements. While a significant fraction of ambient particles were internal mixtures of varying degrees, single particle measurements of chemical composition allowed the identification of time periods during which the ambient ensemble was externally mixed. In some cases the chemical composition of the particles suggested a

likely source. Throughout the full sampling period, the ambient ensemble was an external mixture of combustion-generated HOA particles from local sources (e.g. traffic), with number concentrations peaking during morning rush hour (04:00-08:00 LT) each day, and more processed particles of mixed composition from nonspecific sources. From 09:00-12:00 LT all particles within the ambient ensemble, including the locally produced HOA particles, became coated with NH_4NO_3 due to photochemical production of HNO_3 . The number concentration of externally mixed HOA particles remained low during daylight hours. Throughout the afternoon the OOA component dominated the organic fraction of the single particles, likely due to secondary organic aerosol formation and condensation. Single particle mass fractions of (NH₄)₂SO₄ were lowest during the day and highest during the night. In one instance, gas-to-particle condensation of $(NH_4)_2SO_4$ was observed on all measured particles within a strong SO_2 plume arriving at T1 from the Particles with high NH₄Cl mass fractions were identified during early northwest. morning periods. A limited number of particles ($\sim 5\%$ of the total number) with mass spectral features characteristic of biomass burning were also identified.

The material presented in this chapter has been accepted for publication in *Atmospheric Chemistry and Physics Discussions* as Cross, E.S., Onasch, T.B., Canagaratna, M., Jayne, J.T., Kimmel, J., Yu, X.Y., Alexander, M.L., Worsnop, D.R. & and Davidovits, P. 2008, "Single Particle Characterization Using a Light Scattering Module Coupled to a Time-of Flight Aerosol Mass Spectrometer".

4.2 INTRODUCTION

To accurately model the radiative forcing of aerosol particles, one must measure in real-time the size, shape, density, chemical composition, and mixing state of ambient particles. This is a formidable challenge because the chemical and physical properties of the aerosol particles are highly complex, dependent on the emission sources, the geography and meteorology of the surroundings, and the gas phase composition of the regional atmosphere. As a result, aerosol particles continually change as they are transported through the atmosphere. Without a detailed understanding of the sources and atmospheric processes that control the chemical and physical transformations of the particles, the influence of aerosol particles on climate remains highly uncertain. Currently, uncertainties in the evaluation of aerosol direct and indirect radiative effects are the source of the largest uncertainty in estimating the overall radiative forcing of the climate (*IPCC*, 2007).

Urban areas produce large quantities of aerosol particles together with gas phase precursors that influence secondary aerosol formation. Emissions from the numerous sources within an urban environment cause adverse health effects, reduction in visibility, deposition of chemicals to the ecosystem, and direct and indirect radiative forcing that are evident on local, regional, and global scales (*Molina et al.*, 2007). The MILAGRO (Megacity Initiative: Local and Global Research Observations) field study was conducted in and around Mexico City during March of 2006 (*Molina et al.*, 2008) (http://www.eol.ucar.edu/projects/milagro/). The aim of the study was to obtain a more complete understanding of the atmospheric transformations that occur within the urban plume as it is transported away from the city. The part of the MILAGRO study described

in this chapter focused on the chemical transformations and source apportionment of the aerosol particles.

Until recently, available real-time quantitative instrumentation could provide only an average chemical composition for the ambient aerosol particle ensemble. To evaluate the radiative effects of the aerosol particles and to begin to identify their sources, average data are not necessarily adequate. Consider for example two aerosol particles, one composed of purely carbonaceous material (organic carbon and elemental carbon or soot), and the other composed of purely inorganic material. The hygroscopity, cloud condensation nuclei (CCN) activity, and optical properties of these two (externally mixed) aerosol particles may be significantly different than the hygroscopic, CCN and optical properties of two similar size aerosol particles that are internally mixed (i.e. each particle composed of 50% carbonaceous and 50% inorganic material). Measuring the single particle chemical composition provides the information necessary to determine the ensemble mixing state and analyze the chemical transformations taking place as the particles undergo atmospheric processing. Some of the complexities of particle CCN properties due to coating and mixing are discussed in Sun and Ariya (2006), Petters et al. (2006), and Shilling et al. (2007). The effects on optical properties of particles due to coating, mixing, and aging processes are discussed in Chylek et al. (1995), Fuller et al. (1999), Lesins et al., (2002), Quinn et al. (2005), Baynard et al. (2006), Barnard et al. (2007) and Bond et al. (2006).

A key advance in atmospheric science has been the development of aerosol mass spectrometers that, with on-going improvements and design modifications, can now measure size and chemical composition for individual particles within the ambient ensemble. (For recent reviews see *McMurry et al.*, 2000; *Sullivan and Prather*, 2005, *Murphy*, 2007a; *Nash et al.*, 2006; and *Canagaratna et al.*, 2007.) One example of such an instrument, featured in this chapter, is the aerosol mass spectrometer (AMS) developed by Aerodyne Research Inc. (*Jayne et al.*, 2000).

The AMS instrument measures ensemble average chemical composition and size of submicron particles. Recently, the AMS has been redesigned to incorporate two new features that significantly expand the capability of the instrument to provide single particle information. First, the quadrupole mass spectrometer was replaced by a time-of-flight mass spectrometer (TOFMS) (*Drewnick et al.*, 2005; *DeCarlo et al.*, 2006). With the TOFMS coupled to the AMS, single particle mass spectra can be obtained. (This combined instrument is known as a ToF-AMS.) The ToF-AMS can quantitatively measure particle-by-particle, non-refractory aerosol composition as a function of particle aerodynamic diameter. In 2005, Drewnick and co-workers demonstrated the ability of the ToF-AMS to measure single particle mass spectra.

In the second modification, a light scattering module was integrated into the AMS instrument. This version of the instrument is referred to as the LS-AMS (*Cross et al.*, 2007). The light scattering module provides a single particle measurement of scattered light intensity (R_{LS}) for all particles above $d_p \sim 250$ nm that enter the AMS and impact on the heated vaporizer. A single calibration curve converts R_{LS} to an optical diameter (d_o). Using the relationship between d_o and the simultaneously measured vacuum aerodynamic diameter (d_{va}), the LS-AMS provides a real-time, per particle measurement of the density of the sampled aerosol particles. Further, the LS-AMS provides a quantitative measure of

the internal collection efficiency of the AMS by comparing the number of chemically detected particles to the total number of optically detected particles.

The light scattering module has now been added to the ToF-AMS. In this new instrument combination, the acquisition of mass spectra for each particle is triggered by a light pulse scattered by the particle. This instrument is designated as the LS -ToF-AMS. The LS-ToF-AMS uses thermal desorption and continuous electron impact ionization of single particles, enabling the detection, quantification, and classification of non-refractory, especially organic, fractions of ambient particles. This new approach is unique among current field deployable single particle mass spectrometers, which typically consist of laser-based desorption/ionization instruments that detect refractory material best (e.g. sodium chloride, soot, and dust) (*Murphy*, 2007a; *Nash et al.*, 2006).

The optical triggering improves the effectiveness and efficiency of the AMS as a single particle mass spectrometer by minimizing the number of data files saved and post-processing steps required to identify individual particles. The presence of the light scattering module does not influence the instrument's ability to measure the ensemble average chemical composition and size distribution. Therefore, the LS-ToF-AMS can measure both ensemble average and single particle properties (e.g. mixing state) of the ambient aerosol by alternating data acquisition modes.

In this chapter, we present results obtained with the LS-ToF-AMS during the MILAGRO field study in Mexico City in March 2006. The LS-TOF-AMS was located at the T1 sampling site ~ 40 km NE of the city center. (See the MILAGRO/INTEX-B 2006 special issue of Atmospheric Chemistry and Physics for other results from the MILAGRO field experiment). Typical AMS measurements of submicron, non-refractory

aerosol chemistry and chemically-speciated size distributions were obtained from March 12-30, 2006 with several interruptions due to power failures and instrument calibrations. The LS-ToF-AMS successfully characterized the size, chemical composition, and mixing state of individual particles over a 75-hour period from 04:27 LT on March 27 to 07:24 LT on March 30, 2006. The ensemble average size and chemical composition were also obtained for this period using the same AMS instrument. This chapter highlights the results of the single particle measurements made with the new LS-ToF-AMS instrument combination.

4.2.1 Brief Survey of Single Particle Mass Spectrometry

Most current, successful single particle mass spectrometers use lasers for particle vaporization and ionization. Among these instruments are the Aerosol Time-of-Flight Mass Spectrometer or ATOFMS (*Gard et al.*, 1997; *Su et al.*, 2004), the Particle Analysis by Laser Mass Spectrometry or PALMS instrument (*Murphy and Thomson*, 1995; *Thomson, Schein, and Murphy*, 2000), the Single Particle Laser Ablation Time-of-flight Mass Spectrometer or SPLAT-MS (*Zelenyuk and Imre*, 2005) and the Rapid Single Particle Mass Spectrometer or RSMS-II (*Phares et al.*, 2002). While several instruments employ techniques to separate the vaporization and ionization of single particles (e.g. infrared laser pulse for particle desorption prior to ionizing laser pulse for gas phase ionization), most field deployed single particle instruments use either a single excimer or Nd-YAG laser pulse to both vaporize and ionize single particles. This study represents a new approach to single particle mass spectrometery using the AMS thermal vaporization and electron impact ionization techniques.

Single particle mass spectrometers using laser desorption/ionization methods are difficult to quantitatively calibrate (Murphy et al., 2007a,b). Because the high powered laser has to be tightly focused, the detection and ionization efficiency is highly dependent on the shape and size of the particle. Particles with aspherical shapes tend to generate broad particle beams when sampled into vacuum, even with current aerodynamic lensing technology, and thus laser spot size and distance from inlet can control detection efficiency (Huffman et al., 2005). Further, the wavelength and power of the laser used to vaporize and ionize the particles can bias chemical detection (Nash et al., 2006; Murphy, 2007a). For example, species with relatively low ionization potentials (such as potassium) are preferentially ionized and detected. Difficult to ionize species (such as sulfuric or nitric acid) often evade detection. Perhaps even more importantly, the organic ions generated from most laser-based aerosol mass spectrometers are highly fragmented, in many cases to the point of formation of carbon cluster ions. Such fragmentation limits obtainable chemical information (e.g. C:O ratio, organic species classifications, and elemental carbon versus organic carbon). The measured mass spectrum signal is often non-linear with the mass content of the aerosol particle.

On the other hand, laser ionization single particle mass spectrometers can detect refractory components such as metals, minerals and dust, whereas thermal desorption instruments such as the AMS detect the non-refractory fraction of the sampled particles. Further, some laser-based systems provide high precision vacuum aerodynamic diameter measurements, through the use of two light scattering lasers, and detect significantly smaller particles (>80 nm) by focusing both the light scattering and vaporization/ionization lasers.

The amount of data routinely acquired by any single particle mass spectrometer presents a formidable analytical challenge. For example, Moffet et al. (2008a) acquired 1 million single particle mass spectra over 3.5 weeks of continuous sampling with the laser ablation ATOFMS instrument during the MILAGRO campaign. During the present 75-hour study, the LS-TOF-AMS sampled ~13,000 single particles and collected 46 GB of single particle data, while simultaneously measuring the average size, chemical composition, and mass of the ambient aerosol ensemble.

In experiments using laser ablation mass spectrometers, hierarchical cluster analysis programs are used to interpret the data. Such programs interrogate the chemical composition, and sort the particles into similar and dissimilar clusters with respect to the mass spectral signals (Song et al., 1999; Murphy et al., 2003; Phares et al., 2001). This methodology simplifies the data set so that a small number of measurable parameters, usually the relative intensity of specific ion signals, can characterize a given cluster. For example, Moffet el al. (2008a) characterized the single particle data set obtained with the ATOFMS instrument at the T0 site using the ART-2a clustering algorithm (Song et al., 1999). For this data analysis, a subset of 24,000 sub-micron and 24,000 super-micron particles were analyzed with ART-2a. The resulting clusters were then matched to the rest of the single particle data set (total of 1 million particles). The clustering algorithm generated 60 sub-micron clusters and 200 super-micron clusters that effectively described 88% of the chemically analyzed single particles. Based on similarities in the major ion peaks for different clusters, Moffet then generated 15 general particle types by hand from the original 260 clusters and characterized the single particles with respect to this smaller list. While clustering techniques have proven useful at identifying trace components that may point to particle sources (e.g. metals), it has yet to be shown that laser-based instruments and their clustering analysis techniques can provide quantitative measurements of the composition and mixing state of ambient submicron aerosol particles, which are composed mainly of non-refractory organic, sulfate, and nitrate species.

This chapter describes the first field deployment of a new approach - single particle thermal vaporization mass spectrometry - that may provide useful information on particle chemical compositions, mixing states, and source characteristics that currently cannot be obtained through ensemble measurements or laser-based single particle instruments. Further, the combined LS-ToF-AMS instrument provides a practical method for obtaining to simultaneous ensemble and single particle measurements.

In the AMS instrument, particles impact a heated surface (600 °C) and the vaporized components are ionized by electron impact (70 eV). The AMS measures ion signals that are proportional to the total non-refractory particulate mass and thus, the measured signals can be quantified and apportioned into chemical species. Because the single particle mass spectra are analogous to AMS ensemble mass spectra, they are amenable to the same mass spectral deconvolution techniques currently in use for standard, ensemble AMS data. In particular, the single particle mass spectra can be readily analyzed using the standard AMS fragmentation patterns allowing for the classification and calculation of single particle organic and inorganic mass fractions (*Jimenez et al.*, 2003; *Allan et al.*, 2004). Further, the organic fractions can potentially be analyzed using more complicated, and rich, mass spectral deconvolution techniques, such as Positve Matrix Factorization (PMF) (*Lanz et al.*, 2007; *Lanz et al.*, 2008;).

The current challenges and limitations the LS-ToF-AMS, as deployed in this initial study, are (1) low duty cycle for single particle detection, (2) relatively low signal-to-noise due to high background ion signals in the AMS ionization cage, and (3) the effects of particle bounce prior to complete vaporization of all non-refractory components. Despite these challenges, meaningful single particle chemical and size information was obtained. The results are presented in the context of the contemporary ensemble measurements using standard AMS operational modes. Specifically, information is presented about source characterization, ensemble mixing state and atmospheric processing.

4.3 EXPERIMENTAL METHODS

4.3.1 Instrumentation

4.3.1.1 LS-ToF-AMS

A schematic of the ToF-AMS equipped with the light scattering module was shown in Figure 2-2 in Chapter 2. Individual components of the instrument have been described in other publications (Cross et al., 2007; Jayne et al., 2000; Jiménez et al., 2003; DeCarlo et al., 2006; Drewnick et al., 2005;]. Here we provide a brief overview of the instrument. The LS-ToF-AMS consists of three main sections: (1) aerodynamic lens, (2) particle time-of-flight region, and (3) particle vaporizer together with the TOFMS. As shown in Figure 2-2, the light scattering module is located in the particle time-offlight region between the aerodynamic lens and the vaporizer surface. In the AMS, particles are sampled from ambient pressure (590 torr at T1 in Mexico City) into an aerodynamic lens through a 130 μ m orifice. In their passage through the lens, particles are accelerated by the pressure drop, ~2 torr inside the lens and < 10⁻⁴ torr in the time-of-flight region. The aerodynamic lens focuses particles towards a rotating mechanical chopper, which modulates the particle beam. The chopper is mounted at the front of the particle time-of-flight chamber. The alignment of the 1% chopper slit opening with the particle beam defines t₀ for the particle time-of-flight. At the end of the time-of-flight region, particles impact a heated surface (~ 600°C) and the non-refractory species are flash vaporized. The resulting plume of vapor is ionized by electron impact (70 eV) and the ions are transferred to the TOFMS. Mass spectra are acquired and stored in a manner that depends on the mode of operation of the AMS as discussed in Section 4.3.2.

The light scattering module consists of a diode-pumped 405 nm continuous wave 50 mW laser (CrystaLaser, LC BCL-050-405), external mirrors for alignment of the light beam, an ellipsoidal mirror for scattered light collection (Opti-Forms E103-2-01), a razor blade beam stop for quenching the throughput laser light, and a photomultiplier tube (PMT) for scattered light detection (Hamamatsu H6779-00). An optical scattering signal (R_{LS}) is obtained for nearly every particle that impacts the surface of the vaporizer (3.8 mm in diameter) if the particle is larger than the optical size detection limit, in this case $d_p \sim 250$ nm. As detailed in Cross et al., (2007), this purposeful defocusing of the light scattering laser beam allows for the near complete optical detection of spherical and aspherical particles that impact the vaporizer.

4.3.2 Data Acquisition

Without the light scattering unit, the C-ToF-AMS can operate in three data acquisition modes: Mass Spectrum (MS) mode, Particle Time-of-Flight (PToF) mode, and "Brute Force" Single Particle (BFSP) mode. These modes of operation are described in detail by Drewnick et al. (2005) and DeCarlo et al. (2006). The addition of the light scattering module provides a fourth mode of operation designated as the Light Scattering-Single Particle mode (LSSP). The first two modes are ensemble aerosol measurements, whereas the latter two are single particle modes of operation. The first three modes of operation will be discussed here briefly, the fourth mode will be discussed in greater detail.

During MILAGRO study, the LS-TOF-AMS instrument was sequentially operated in the three modes; MS, PTOF, and LSSP. The sampling time periods for each mode were set corresponding approximately to their duty cycles. The aerosol mass spectrometer measurements presented in this chapter were saved in 5 min intervals. At the conclusion of each saving interval, one PToF file, one MS file, and one LSSP file was saved. During the first 150 s of the saving interval, the instrument was alternated every 10 s between MS and PToF modes. During the second 150 s, the instrument was operated in LSSP mode. During each LSSP saving interval, 15 to 30 single particles were sampled (data transferred and saved) depending on the ambient particle concentration. By comparison, in the PToF mode, chemical signals from ~ 2000 particles were averaged during each 75 s PToF sampling period and ~ 50,000 particles were averaged in MS mode.

4.3.2.1 Mass Spectrum (MS) and Particle Time of Flight (PTOF) Modes

As described previously, the TOFMS in the ToF-AMS instruments is a pulsed, orthogonal extraction time-of-flight mass spectrometer. The pulsers were operated at 56 kHz during the MILAGRO study. Thus, the measure of ion signals (i.e. molecules or mass) is determined as a flux of ions in time, similar to the quadrupole aerosol mass spectrometer, rather than the integral of ions from a single event, such as the ablation and ionization of a single particle in a laser-based aerosol mass spectrometer. In the MS mode, the chopper is alternately closed (blocking the particle beam) and opened (typically on a time scale of a few seconds) and full mass spectra are acquired and averaged for each time period. The difference in the ion signals acquired at each m/z in the open and closed periods provides the difference mass spectrum for the particle ensemble.

In the PTOF mode, the chopper wheel rotates at a frequency of 130 Hz. During each chopper cycle (i.e. slit to slit), particles enter the time-of-flight chamber through one of two slits in the chopper wheel. The two slits together comprised 1% of the total chopper area. Thus the sampling duty cycle in the PTOF mode is 10^{-2} . A single PTOF data file consists of 300 mass spectra acquired during the ~ 6 ms of sampling time during a given chopper cycle (each mass spectrum is acquired in 18 ms). Particle velocity is obtained from the measured time interval between the chopper slit opening (t_0) and chemical ion signal (t_0) provided by the vaporized and ionized particle. The vacuum aerodynamic diameter is calibrated using techniques described in Jayne et al. (2000). In the PTOF mode, particles impact the vaporizer surface individually; however, signals are averaged over many chopper cycles so that average, size-resolved, chemically-speciated mass distributions are obtained.

4.3.2.2 Brute Force Single Particle (BFSP) Mode

The BFSP mode of ToF-AMS operation is similar to the PTOF mode, except that instead of averaging mass spectra from multiple chopper cycles, the series of 300 mass spectra for each chopper cycle are saved individually. Because the size of the data files saved during BFSP mode (dependent upon # of chopper cycles saved) are significantly larger than the files saved in MS and PTOF modes, it is important to review the mechanism of filtering and saving particle information during single particle experiments.

Without a light scattering module, single particle data be can saved in one of two ways: 1) mass spectra are saved for all chopper cycles regardless of whether a particle entered the AMS during the chopper period or 2) mass spectra are saved only for single particles producing a pre-set sufficiently high chemical ion signal. The former method requires extensive post-processing of large data sets that are mainly zeros. Because the second method depends on setting a threshold for specific m/z signals, chemical detection biases can be introduced if the composition of the particles is unknown.

The BFSP mode has been used for instrument calibrations and other laboratory experiments with well-defined particles such as ammonium nitrate particles. The practical application of the AMS as a true single particle instrument for measuring ambient particles required the development of a LSSP mode.

4.3.2.3 Light Scattering Single Particle Mode (LSSP)

The LSSP mode offers three distinct advantages over the BFSP mode in measuring the mass spectra of single particles. First, instead of saving mass spectra for every chopper cycle (as in the BFSP mode, option 1), the LSSP mode saves mass spectra only if a light scattering pulse is observed during that chopper cycle. Second, the optical diameter and the vacuum aerodynamic diameter of each particle are measured and from these two parameters, the effective density and total particle mass can be calculated for each particle, independent of the mass spectrometer measurements. Third, the arrival time of the particle at the vaporizer surface can be calculated from the measured particle time-of-flight between the chopper slit and scattered light pulse. This measurement provides information about the efficiency and time-scale of the vaporization/ionization process for each sampled particle.

The two disadvantages of the early version of the LSSP mode used during MILAGRO were (1) only particles larger then a optical detection limit of $d_p \sim 250$ nm were detected and (2) the actual duty cycle of the LSSP mode as deployed in Mexico was very low, only about 10⁻⁴ (see below). The first issue was not significant because the LS-ToF-AMS instrument deployed at T1 in Mexico City had a chamber background that limited single particle chemical detection (for an adequate number of m/z signals) to approximately the same $d_p \sim 250$ nm optical diameter threshold (See Figure 4-4 in Section 4.4.2).

The low duty cycle was due to the fact that the light scattering signal was collected in the second 2 GHz DAQ channel to ensure direct correlation with the mass spectral signal for each particle. Thus, a significant fraction of the LSSP mode duty cycle was due to transferring and saving the data. This is evident from the following quantitative considerations. The time required to transfer and save the large amount of data obtained for a single particle in the LSSP mode during MILAGRO was about 800 ms. One chopper cycle was about 7 ms. Therefore, the sampling duty cycle of the PToF

mode was reduced by about 10^{-2} yielding a LSSP duty cycle of about 10^{-4} . As a consequence, the LSSP data obtained during the 75 hour sampling period contains 10^{4} fewer particles than the MS mode data (~ 3000 particles compared to $3x10^{7}$ particles). The efficiency of the LSSP mode of operation is being improved in the second generation of the LS-ToF-AMS.

The optical detection limit, as deployed in Mexico City, was a single value that was conservatively chosen to ensure that all saved data represented real particles. Each time the light scattering signal triggered a save, 300 mass spectra and the corresponding light scattering signal were transferred from the DAQ board and saved to the hard drive in binary format. Post-processing algorithms were developed to correlate in time the light scattering pulse and chemical ion pulse and to integrate the total ion signal at each m/z for the ions produced by the vaporization-ionization of each single particle. Each m/z signal of each single particle mass spectrum had separate baseline and signal-to-noise levels that required attention; m/z-specific thresholds were derived from signal levels prior to the particle's vaporization and ionization event to identify real particle ion signal from background noise levels. To ensure single particle data quality, multiple consistency checks were done as described in Section 4.4.

Although this preliminary deployment of the LS-ToF-AMS was hindered by low duty cycles and thus low number of single particle recorded events, the data obtained is shown to be useful in determining the mixing state, monitoring the chemical transformations due to atmospheric processing and identifying sources of the particulate matter in Mexico City during the 75 hours of single particle data collection. Future implementations of the LS-ToF-AMS DAQ hardware and software are planned that will increase the duty cycle of the LSSP mode by about a factor of 10.

4.4 SINGLE PARTICLE ANALYSIS

In our current study, about 13,000 single particle mass spectra were recorded and analyzed during the 75-hour sampling period. The following information was obtained for the individual particles: vacuum aerodynamic diameter (d_{va}), optical diameter (d_o), and chemical composition. Multiple internal consistency checks were performed on the single particle data to ensure the data acquisition and processing quality. The correlated single particle measurements of d_{va} , d_o and chemical ion signals provided comparison between two independent measures of total particle mass. The chemical compositions of the single particles were analyzed using standard AMS analysis techniques. Knowing the sampling duty cycles for the LSSP and PTOF modes allowed a direct comparison between the average LSSP and PTOF mass distributions and tested the capability to measure single particle chemical compositions (i.e. mass fractions). In a few cases two particles of distinct composition and size entered the AMS during a single slit opening. The observation of particle coincidence in the system demonstrated the capability and power of the LS-ToF-AMS to determine the mixing state of ambient aerosol.

4.4.1 Single Particle Collection and Detection

It has been demonstrated that the AMS does not detect all non-refractory particles that impact the vaporizer surface most likely because the particles bounce off the heated surface without vaporizing (Matthew et al., 2008). Laboratory experiments show that the collection efficiency is a function of the particle composition and phase. For example, laboratory-generated particles composed of liquid organics or ammonium nitrate are detected with 100% efficiency. On the other hand, laboratory generated dry ammonium sulfate particles are collected with only ~25% efficiency. The collection efficiency of the AMS in sampling ambient aerosol particles has been reported to be ~ 0.5 (*Alfarra*, 2004; *Drewnick et al.*, 2004; *Hogrefe et al.*, 2004; *Takegawa et al.*, 2005; *Zhang et al.*, 2005a). This mass-based collection efficiency was obtained by comparing the non-refractory mass (typically sulfate) measured by the AMS to the mass collected by co-located instruments such as a Particle-into-Liquid-Sampler (PILS). The collection efficiency of the LS-TOF-AMS used during the MILAGRO campaign was also determined to be ~0.5 by comparisons with co-located SMPS-derived mass distributions and black carbon measurements, and with direct comparison with Aerodyne's C-ToF-AMS on the mobile laboratory during a two day T1 visit (*Herndon et al.*, 2008).

The light scattering module counts and optically sizes all particles of diameter greater than $d_p \sim 250$ nm whether they produce a chemical ion signal or not. By comparing the total number of chemically detected particles to the total number of optically detected particles, a count-based, self-contained collection efficiency for the AMS is obtained.

During the 75-hours of single particle sampling, ~ 49% of all optically detected particles produced a measurable chemical ion signal while the remaining ~ 51% did not produce a clearly detectable chemical signal. This count-based collection efficiency is close to the mass-based collection efficiency of ~ 0.5. However, we note that the countbased and mass-based collection efficiencies do not provide identical mesurements. The optical module detects both refractory and non-refractory particles ($d_p > 250$ nm) while the mass-based measurement detects only the non-refractory material within ambient particles (30-1000 nm d_{va}).

Because the time-of-flight between the chopper opening and the optical scattering signal is measured in the LSSP mode of operation, additional important information about the nature of the particle vaporization-collection process is obtained. Specifically, this measurement allows one to calculate the arrival time of each particle at the vaporizer surface. In this way, the calculated arrival time of the particle at the vaporizer and the observed time of the chemical ion signal can be compared. Based on this comparison, particle vaporization can be separated into three categories: prompt, delayed, and null vaporization events. Prompt particle events are those that produced a chemical ion signal within 200 µs of impacting the vaporizer surface. The 200 ms limit was chosen based on the timing uncertainty due to the chopper slit width (~70 ms) and the possibility that particles may strike the inverted cone shaped vaporizer more than once prior to full vaporization. Delayed particle events produce a chemical ion signal peak $> 200 \ \mu s$ after the calculated arrival time at the vaporizer. Clearly, these delayed particles do not vaporize upon initial impact with the heater, but most likely bounce and then vaporize upon secondary impacts with hot ionizer cage surfaces. In the null events, particles strike the vaporizer surface but do not produce a clear chemical ion signal. On a particle by particle basis, the chemical ion signals produced by null particle events are nearly indistinguishable from the mass spectrometer noise. However, when averaged, the total ion signal contribution from the null events is a few percent of the total. In the Milagro study the number fractions of the prompt, delayed, and null particle events were 0.23,
0.26, and 0.51, respectively. The prompt particles contained 59% of the total measured single particle mass, whereas the delayed and null particles contained 38% and 3%, respectively.

The chemical detection collection efficiency results show a slight particle size dependency. Figure 4-1 shows the number-based collection efficiencies as a function of particle time-of-flight (proportional to d_{va}) for all the particles detected. The fraction of prompt particles detected decreases with increasing particle size (d_{va}), while the fraction of delayed particles increases with increasing particle size. These inversely related results appear to indicate that larger particles are more prone to bounce prior to full vaporization, likely due to greater momentum of the larger particles. The null particles constituted the largest fraction of the total particles detected and also exhibited a size-dependency similar to the delayed fraction, with greater number of null particle events for larger particles.



Figure 4-1. Total particle counts (in grey) and number fractions of prompt (blue), delayed (green) and null (black) particles as a function of time-of-flight (i.e. d_{va}).

The percentage of the total particle mass (from chemical ion signals) detected from the prompt particle events was, on average, higher than that from particles with delayed vaporization. This is illustrated in Figures 4-2a and 4-2b that show the measured single particle mass obtained via calibration from the sum of all ion signals measured with the mass spectrometer for prompt and delayed particles respectively. In each plot, the mass obtained from the chemical measurement is plotted against the single particle mass (m_p) derived from the measured d_{va} and d_o : $m_p = \pi/6 \times d_o^2 \times d_{va}$. The HOA mass fraction of each particle is shown by the color of the data points in each figure.



Figure 4-2. Measured single particle mass obtained from chemical ion signals plotted versus single particle mass obtained from optical diameter (d_o) and vacuum aerodynamic diameter (d_{va}) measurements for (a) particles with prompt vaporization and (b) particles with delayed vaporization.

The data displayed in Figure 4-2a and 4-2b show considerable scatter due to measurement uncertainties discussed below in Section 4.4.1.1. Still, certain features are clearly evident. As is shown in Figure 4-2a for the prompt vaporization events, the two independent measures of single particle mass are clustered near the 1:1 line. A linear fit of the data yields slope of 0.81 (intercept < 2 femtograms; $R^2 = 0.5$). The data in Figure

4-2a exhibit a significant scatter that is correlated with the HOA mass fraction in the particle. The ensemble HOA mass fraction (discussed further in Section 4.5.2) is correlated in time with particulate elemental carbon and gas phase CO measurements. These correlations, together with other published observations (*Canagaratna et al.*, 2004; *Zhang et al.*, 2005b; *Zhang et al.*, 2005c), indicate that HOA containing particles typically contain fractal-like elemental carbon cores. This nonspherical, refractory material does not produce a chemical ion signal in the AMS and reduces the reliability of the d_o measurement due to shape and light absorption. Removing the particles with HOA content (>10%), increases the slope (0.88) and R² (0.57) of the linear fit.

The data obtained from the delayed vaporization events are shown in Figure 4-2b. This set of data exhibits significantly larger scatter and lower overall chemical ion signals than obtained from the prompt vaporization events. A linear fit to the data in Fig. 3b has a slope of 0.41 ($R^2 = 0.12$), suggesting that the measured chemical ion signals represent only about ~40% of the total particle mass. It is likely that particles with delayed vaporization have struck at least two heated surfaces inside the AMS detection region (the vaporizer being the first) and in most cases were not completely vaporized within the 6 ms particle time-of-flight detection window. Speculations can be put forth why some particles vaporize promptly and fully while others do not. At this point however, the phenomenon remains unexplained. Partial vaporization makes chemical identification of such particles uncertain. Therefore, in the Results and Discussion Section (Section 4.5) we will focus only on the particles that had prompt vaporization.

4.4.1.1 Uncertainty in Single Particle Mass Measurements

Figures 4-2a and 4-2b exhibit significant scatter that is attributed to uncertainty in the measurements of chemical ion signal, dva and do. The standard deviations determined from the binned data are approximately 43%. Uncertainty in the chemical ion measurement was determined by analyzing the single particle response of the instrument to known size ammonium nitrate and di-octyl sebacate particles. In laboratory calibration experiments, the variance in single particle ion signal (sum of nitrate ions and organic ions for each particle) for the two different particle types was found to be $\pm 10\%$. The signal-to-noise from the single particle chemical ion signals made during the MILAGRO study were further limited by rather high chamber background signals during the field deployment (single particle chemical ion signals are difference measurements).

The diameter-derived particle mass is influenced by uncertainties in the d_{va} and d_o measurements. Uncertainty in the d_{va} is due to the timing uncertainty from the 1% chopper. With a 1% chopper slit and a chopper frequency of 130 Hz, the timing uncertainty is ~ 70 µs which corresponds to a maximum uncertainty in d_{va} of 13%. Uncertainty in the d_o determination is caused by two factors. First, the spread in the light scattering signals caused by some particles passing through the center and others through the edges of the laser beam (laboratory studies have shown that spherical particles exhibit 11% uncertainty in scattered light signal; nonspherical particles will exhibit a higher uncertainty). Second, the calibration curve used to convert scattered light into an optical diameter is based on NH₄NO₃ particles. For particles with a refractive index that is different from the refractive index of NH₄NO₃, an uncertainty in d_o is introduced. For the range of refractive indices expected in the MCMA (real refractive indices of 1.4 – 1.6 [*Seinfeld and Pandis*, 2006]), the uncertainty in d_o is ~ 10% (*Cross et al.*, 2007). The

uncertainties in d_o due to refractive index and particle position in the laser each get doubled in the conversion to particle mass, causing the overall uncertainty in optical diameter derived mass to be ~ 40%. This uncertainty is an underestimate due to the known presence of black carbon particles, which absorb light at $\lambda = 405$ nm (the λ of the detection laser in the LS-ToF-AMS). The uncertainty in the diameter-derived mass likely accounts for much of the variance in Figures 4-2a and 4-2b. Variations in the diameterderived single particle mass will not affect the measurement of single particle chemical composition.

4.4.2 Single Particle Chemical Composition

Single particle mass spectra were analyzed using the standard AMS approach based on a priori information of the fragmentation patterns of inorganic and organic species (*Allan et al.*, 2003). This technique identifies inorganic species (ammonium, nitrate, sulfate, and chlorides) and separates their mass spectral signals from particulate organic signals.

The mass spectra of the organic fraction are more complex and require more rigorous deconvolution techniques. Because the single particle mass spectra are analogous to AMS ensemble mass spectra, they are in principle amenable to more complicated mass spectral deconvolution techniques currently being developed and applied to standard AMS mass spectra. These techniques include principle component analysis (PCA) (*Zhang et al.*, 2005b) and positive matrix factorization (PMF) (*Lanz et al.*, 2007; *Lanz et al.*, 2008; *Ulbrich et al.*, 2008). Two of the major types of organic species identified through the use of these multivariate analysis techniques are

oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA). HOA particles are strongly correlated with primary aerosol originating from fossil fuel combustion sources. The OOA particles are most likely secondary organic aerosol (SOA) formed in the atmosphere through the condensation of oxidized low vapor pressure organic gases. These techniques are currently being extended to refine and identify other important mass spectral markers for organic species; for example, biomass burning spectral markers.

The first AMS measurements that separated OOA and HOA were preformed by Zhang et al. (2005b) in the Pittsburgh, PA field study. In those experiments, Zhang and co-workers found a simplified two-component analysis wherein the total mass concentration of organics could be reproduced by a linear combination of mass signals at mass-to-charge ratios m/z = 44 (mostly CO_2^+) and m/z = 57 (mostly $C_3H_9^+$). The m/z 44 signal is associated with OOA compounds and the m/z 57 is associated with HOA compounds. An expanded multi-component version of this technique has been applied to more than 30 AMS data sets obtained throughout the Northern Hemisphere midlatitudes (Zhang et al. 2007). More recently, using Positive Matrix Factorization (PMF), Lanz et al. (2008) and Ulbrich et al. (2008) extended the 2-factorial approach to apportion ambient organic aerosol matter into two classes of oxygenated organics.

Our initial chemical analysis approach was to conduct PMF analysis on the ensemble aerosol mass spectra (MS Mode), ensemble PTOF distribution mass spectra, and single particle mass spectra. However, due to low S/N for signal at each m/z and low single particle counting statistics for the single particle data and PTOF size distribution data we have settled on the simple and published method for apportioning the organic

fractions into two dominant components using the high S/N m/z's 44 and 57 which have been shown to be the predominant signatures of distinct types of organics, labeled OOA and HOA, respectively (*Zhang et al.*, 2005b). For the ensemble average mass spectra obtained in MS Mode, PMF analysis is used to identify the different organic components.

Comparisons between the 2-factor PMF and 2-component PCA results indicate the both of these methods derive very similar HOA and OOA factors from the ensemble organic aerosol mass spectra, which account for >90% of the variance in the data. Thus, comparisons between the PCA and PMF derived HOA and OOA factors in aerosol loading, size distribution, and single particle measurements are meaningful. Comparisons between two and three factor results for PMF analysis of the ensemble aerosol mass spectra show that a third identified PMF factor is essentially split from the existing HOA component. This third identifiable factor is distinct from the HOA and OOA mass spectra in that it contains significant signal at m/z's 60 and 73. As described in DeCarlo et al. (2008), m/z 60 and 73 are good markers for biomass burning aerosol in Mexico City. Thus, for the purpose of this paper, this third factor will be labeled BBOA (biomass burning organic aerosol). The filter used to identify BBOA single particles is described in Section 4.5.3.1.

Figure 4-3 shows the average single particle mass spectra for the HOA and OOA components (top panels; 4-3a and 4-3b, respectively) and the corresponding PMF factors for HOA and OOA (bottom panels; 4-3c and 4-3d, respectively) from the ensemble analysis. Visual comparison shows a good correlation between the average HOA and OOA mass spectra obtained with the two different deconvolution methods.



Figure 4-3. Average HOA and OOA organic mass spectra obtained from ambient ensemble measurements using PMF analysis (upper region, plots a and c) and two-component PCA analysis (lower region plots b and d).

A comparison of three OOA and three HOA single particle mass spectra is shown in Figure 4-4. The particles were randomly chosen from the sampled particles with the criterion that the particle contains a high organic mass fraction consisting of either OOA or HOA. This figure demonstrates the following features: a). Single particles with d_o ~350 nm (300 < d_{va} < 700 nm; note, d_{va} is a function of particle density) exhibit relatively high S/N for all m/z signals < 100 amu. b). HOA and OOA particles are readily distinguishable and exhibit characteristic peaks for HOA (m/z 57) and OOA (m/z 44 and 18). c). Single particles with d_o ~200 nm (or smaller) (250 < d_{va} < 350 nm) have low S/N at most m/z's and the single particle mass spectra exhibit only a few characteristic m/z ion signals. Thus, the size detection limit for single particle chemical ion and optical measurements was approximately the same for the instrument in the present MILAGRO study.



Figure 4-4. Six single particle mass spectra obtained for three different sized organic particles ($d_o \sim 200$, 250, and 350 nm) predominately composed of HOA (a-c) and OOA (d-f) components. Particle d_{va} , d_o , and mass are shown in the insert.

4.4.3 Comparison of Single Particle and Ensemble Measurements

In Figure 4-5a we show mass spectrometer ion signals (Hz) as a function of particle time of flight. The ensemble averaged signal (PTOF mode) is shown as a dashed line and the averaged single particle signal (LSSP mode) is shown in red. The size

detection limits are evident in Figure 4-5a. In the MILAGRO study the LSSP mode detected particles with diameters larger than $d_p \sim 250$ nm ($d_{va} \sim 350$ nm or $\sim 3.1 \times 10^{-3}$ s), whereas the ensemble averaged PTOF signal measured particles down to $d_{va} \sim 30$ nm (with arrival times at the vaporizer $\sim 1.5 \times 10^{-3}$ s or greater). This lower size limit is determined by the transmission cut-off for the aerodynamic lens inlet. The single particle signal is subdivided into ions counts obtained from prompt (blue), delayed (green), and null (black) particles. For particles larger than $\sim d_{va} = 350$ nm (3.1 ms time-of-flight) the signal measured in the PToF mode is in good agreement with the total signal measured in the LSSP mode. This agreement is shown quantitatively in Figure 4-5b which displays the correlation between the LSSP and PTOF signals for arrival times between 3.1 -5.5 ms (data between arrows in Figure 4-5a). The correlation is linear with a slope of 0.85, indicating that the LSSP mode collected 85% of the PTOF signal.



Figure 4-5. (a) Average mass distributions as a function of particle time-of-flight for ensemble data (dashed black line) and total single particle data (red line). Distributions for prompt (blue), delayed (green) and null (black) particles are also shown. (b) Correlation plot between the average PToF and total single particle mass measurements for times-of-flight between 3.1-5.5 ms, denoted with arrows in (a).

We note from Figure 4-5a and 4-5b that the LSSP signal is about 15% smaller than the than the signal obtained in the PTOF mode. The missing 15% is likely due to delayed vaporization of particles smaller than the optical size detection limit and therefore are not detected in the LSSP mode. This interpretation is further supported by the fact that at longer times-of-flight (> 4.8 ms in Figure 4-5a), the average LSSP and PTOF modes agree fully.

The results in Figure 4-5a suggest that the PTOF mode provides an accurate measure of the rising edge of ambient particle mass distributions (i.e. at small particle sizes); however, the PTOF mode broadens ambient mass distributions to larger particle sizes due to delayed particle vaporization events.

A consistency check on the measured single particle chemical compositions was done by comparing the averaged single particle chemical compositions with the chemical compositions measured in PTOF mode (for signal with $d_{va} > 300$ nm). The comparison was performed for organic, nitrate, sulfate, and chloride mass fractions. In all cases, the average chemical composition of the single particle and ensemble PTOF data were the same within experimental uncertainty (+/- 10%).

4.4.4 Mixing State Determination

To illustrate the physical and chemical information obtained with the LS-ToF-AMS, we examine a case when two particles entered the AMS during one chopper opening, recorded at 5:35 LT on March 27^{th} – during the morning rush hour. (Under the ambient particle concentrations observed during the experiment, we expect such a twoparticle coincidence to occur ~ 1% of the time). The top panel of Figure 4-6 shows the scattered light pulses from the two particles as a function of time-of-flight, with t_0 defined by the opening of the chopper slit. The middle panel shows the corresponding chemical ion signals. The lower panel displays the mass spectrum for each of the sampled particles



Figure 4-6. Light scattering signals (upper panel) and chemical ion signals (middle panel) as a function of particle time-of-flight for a single chopper cycle in which two particles entered the LS-ToF-AMS. The lower panel displays the mass spectrum of each particle.

The single particle mass spectra in bottom of Figure 4-6 clearly show that the chemical compositions of the two sampled particles are distinct. Particle 1 is composed of 100% organic material. The largest mass spectrum component is at m/z = 57 characteristic of an HOA particle. Particle 2 is a mixture of oxygenated organics, ammonium nitrate, and ammonium sulfate approximately in equal amounts. The observation of two distinct particle types within the same chopper cycle indicates that the

ambient ensemble was externally mixed during this sampling period. Table 1 summarizes the measured chemical and physical properties for these two particles.

The chemical ion pulses in the middle panel of Figure 4-6 are separated in time because the particle exit velocities out of the aerodynamic lens are substantially different due to the difference in effective densities of the two particles. Particle 1 exits the lens with a velocity of 106 m/s and particle 2 with a velocity of 94 m/s. The time separation between the chemical pulses is greater than the time separation between the optical pulses (324 μ s versus 198 μ s). This difference is due to the additional distance between the laser and vaporizer surface traveled by the two particles. Differences in the vaporization times of the two particles may also influence this time separation (*Cross et al.,* 2007). The ion extraction time is negligible.

The single particle data also provide information about the mass and density of each particle. The mass of particles 1 and 2, as measured by the calibrated mass spectrometer, is 18.2 fg, and 13.0 fg respectively. The mass composition of particles 1 and 2 (using average densities for the components) yields densities of 0.9 g/cm³ and 1.5 g/cm³ respectively. Assuming that the particles are spherical and that all the material in the particles is detected by the mass spectrometer, we calculate the physical diameter of the particle 1 and 2 to be 326 nm and 211 nm respectively.

The amplitudes of the optical scattering pulses shown in the top panel of Figure 4-6 can be used as an independent measure of the particle diameter (denoted as optical diameter d_o). Using the calibration procedure described in Cross et al., (2007) the optical diameters for particle 1 and 2 are 301 nm and 263 nm respectively. This is within 8% and 20% of the diameters obtained via the mass-density calculations.

An independent calculation of the particle density is obtained from the ratio of the vacuum aerodynamic diameter (d_{va}) and the optical diameter (d_o) . That is, $\rho_{eff} = d_{va}/d_o$. The d_{va} is a function of the physical diameter, the material density, and the shape of the particle. The d_{va} values for particles 1 and 2 are 287 nm and 446 nm respectively, obtained from the measured particle velocity via a four parameter empirical fit function as described in Bahreini et al., (2003). The densities derived for particles 1 and 2 using the relationship $\rho_{eff} = d_{va}/d_o$ are 0.95 g/cm³ and 1.7 g/cm³ respectively, in reasonable agreement with the chemically-derived densities.

Combining the chemical and physical information collected by the LS-ToF-AMS from these two particles tells a self-consistent story. Particle 1 was composed of hydrocarbon-like organic matter and exhibited a low effective density. The low effective particle density is consistent with hydrocarbon-like organic (e.g. lubricating oil) densities as well as possibly indicating that Particle 1 was aspherical due to an underlying fractal-like black carbon core. Thus, particle 1 can be identified as a pure HOA particle likely generated from a local combustion source. In contrast, Particle 2 was composed of highly oxidized inorganic and organic matter and exhibited a relatively high effective density consistent with the particle's significant inorganic composition. Particle 2 was an internally mixed accumulation mode particle that likely had undergone significant atmospheric processing prior to detection with the LS-ToF-AMS. The simultaneous observation of these two externally mixed particles illustrates the capabilities of the LS-

ToF-AMS technique to provide a measure of the mixing state and atmospheric processing of ambient submicron aerosol particles.

4.5 RESULTS AND DISCUSSION

A unique feature of the LS-ToF-AMS is that it provides ensemble as well as single particle measurements. In this section, the composition of the ensemble and single particles measured during the MILAGRO field study are presented and discussed. Information from the two data sets are combined to provide a more complete description of the size, chemical composition, transformations, and mixing state of the ambient aerosol in the Mexico City Metropolitan Area.

4.5.1 Sampling Site and Meteorology

The T1 sampling site was located at Tecamac University (19.703 N Latitude and 98.982 W Longitude) at an elevation of 2273 m, ~ 40 km NE of the Mexico City metropolitan area (MCMA). T0 was the site within city center and T2 was located 35 km N-NE of T1. The location of these three field sites was chosen such that each would intercept the MCMA plume as it is transported away from the city center to the North (*Doran et al.*, 2007). The area surrounding T1 consists of built up, highly populated residential neighborhoods and less developed regions with open fields. The residential regions are to the south and east of T1. The less developed areas are toward the north and west. A major commuting highway between Mexico City and Pachuca is ~ 1 km to the east of the site. The LS-ToF-AMS operated in combined single particle and ensemble aerosol modes from March 27 to 30, 2006. The meteorology in the Mexico City basin

during these three days was influenced by a "cold-surge" or "Norte" event on March 23, 2006 that brought higher humidities and westerly winds to the Mexico City basin. The mornings at T1 were clear, the afternoons partly cloudy with isolated convection and precipitation events, and the ground level winds favorable for transport from the city center to T1 (*Fast et al.*, 2007 and *de Foy et al.*, 2008).

4.5.2 Aerosol Ensemble Properties

The time series of average ensemble mass concentrations separated into organic, nitrate, sulfate, ammonium, and chloride components are plotted in Figure 4-7a. As discussed in Section 4.4.2, the measured organic mass was further separated into HOA, OOA, and BBOA components using PMF. The time series for each PMF component is plotted in Figure 4-7b. Diurnal plots each species are provided in Figures 4-7c and 4-7d.



Figure 4-7. Average ensemble mass concentrations (measured in MS mode) as a function of sampling time. (a) Organic components obtained from PMF analysis – OOA, BBOA, and HOA. (b) Chemical components obtained from traditional AMS fragmentation patterns – organic, nitrate, sulfate, ammonium, and chloride. Average diurnal cycles, for the full 75 sampling period, of each chemical component are displayed in plots (c) and (d).

The particulate chemical composition and size distribution reflect both the influence of local sources and intense secondary aerosol production. During the day, the ensemble data show three broad features in the organic particulate matter. The first peak occurs during the early morning (4:00-9:00 LT) and is characterized by HOA and BBOA organic compositions. The second peak occurs between 9:00-12:00 LT and consists of a

strong particulate nitrate signal combined with HOA, BBOA, and OOA organic contributions. During this time the HOA signal was declining rapidly while the BBOA and OOA signals were increasing. The third broad feature occurs throughout the afternoon and is characterized predominately by OOA organics.

In addition to the ensemble average mass concentrations measured in MS mode, average size distributions for the major chemical species were obtained while operating the instrument in PTOF mode. The average vacuum aerodynamic diameter size distributions of all the significant non-refractory components are shown in Figure 4-8a. These components are: organics, nitrate, sulfate, ammonium, and chloride. The inorganic distributions overlap and appear within the accumulation mode size range, centered at d_{va} \sim 350 nm. The organic size distribution is broader than the inorganic distributions. This difference is attributed to the multiple components of the organic mass. To show this more clearly, in Figure 4-8b we plot the HOA and OOA organic components separately (See Section 4.4.2). The HOA distribution is shifted toward smaller d_{va} values compared to the distributions of all other components. This is likely due to the low material density (~ 0.9 g/cm³) and potentially non-spherical shape of HOA particles. (Recall d_{va} is proportional to particle density.) By contrast, the density of OOA particles is typically higher (1.3-1.5 g/cm³) and these particles tend to be more spherical resulting in larger d_{va} These two size modes have been classified previously as the 'traffic' and values. 'accumulation' modes, respectively (Canagaratna et al., 2007). Because of the overlap between their respective size distributions, it is often assumed that the OOA particles are internally mixed with the inorganic species. On the other hand, based on the difference in their size distribution, the HOA particles are usually assumed to be externally mixed with respect to the inorganic and OOA species.



Figure 4-8. Average ensemble mass distributions (measured in PTOF mode) as a function of vacuum aerodynamic diameter (d_{va}) for (a) HOA and OOA components and (b) organic, nitrate, sulfate, ammonium, and chloride.

It is important to note that with only ensemble average size distributions available, the mixing state of the ambient ensemble is assumed, not directly measured. For the particle size-range detected in the LSSP mode (particles with $d_p > 250$ nm) the single particle data unambiguously show whether the ambient ensemble is externally or internally mixed. Section 4.5.4 describes the mixing state of the ensemble based on the measurements of single particle compositions.

4.5.3 Single Particle Chemical Compositions\

The AMS measures only the non-refractory chemical composition of submicron aerosol particles. In order to limit any potential effects of particle bounce, prior to full vaporization of the non-refractory component of single particles, we have chosen to analyze only the prompt vaporization single particle events (refer to Section 4.4.1). Comparing the single particle mass measured by chemical ion signals with the mass derived from d_{va} and d_o measurements indicates that approximately 88% of the single particle mass is accounted for by the chemical ion signals (Figure 4-2a). The remaining $\sim 12\%$ may be due to refractory material (dust, metals, black carbon, etc.) that the AMS does not measure. While inter-particle variations in this analysis are large, the results are consistent with the total PM composition measurements in the MCMA. Salcedo et al. (2006) reported ~20% of the PM_{2.5} measured near the center of Mexico City in 2003 was refractory material (black carbon and soil). Stone et al., (2008) reported that $\sim 25\%$ of the measured PM_{2.5} carbonaceous material at the T1 site was EC during the period of single particle sampling. Stone (2008) also noted that wind-blown dust and soil were present at T1 as potential sources of particles. Typically, dust and soil particles fall into the super-micron size range, which is not detected with the AMS due to transmission efficiency losses for larger particles (Lui et al., 2007).

As was mentioned in Section 4.4.2, several techniques have been developed to obtain the chemical composition of the aerosol particles from their mass spectral measurements. In the current analysis the mass spectra of the non-refractory aerosol composition were initially separated into organic and inorganic species using the method of Allan et al. 2003. The organic fraction was separated into HOA and OOA components using the simple two component PCA algorithm of Zhang et al., (2005b).

In addition to the HOA and OOA anlysis, we explored other single particle filters based on specific m/z signals in the mass spectra that identify unique particle types. For example, several organic particles were observed that were dominated by unique organic m/z signals at m/z = 69, 119, and 169. The spectra, not shown, matched previous examples of high temperature lubricating oil (such as Fomblin pump oil), likely from an instrument pump used at the T1 site for sampling purposes. Fifteen Fomblin particles (0.5% of the particles) were identified. These particles were removed from further analysis. An additional single particle filter was used to identify single particles characteristic of biomass burning organic aerosol (BBOA).

4.5.3.1 Biomass Burning Organic Aerosol (BBOA) Particles

Specific attention was paid to the identification of biomass burning particles. Several published accounts of strong biomass burning influence in the Mexico City basin during the MILAGRO study suggest that biomass burning is an important source of particles in this region (DeCarlo et al., 2008; Yokleson et al., 2007; Moffet et al., 2008a). To investigate potential signatures of biomass burning in the single particle mass spectra, a single particle filter based on m/z marker peaks at 39 (potassium) and 60 and 73 (levoglucosan) was used (DeCarlo et al., 2008; Alfarra et al., 2007; Schneider et al., 2006). Levoglucosan (1,6-anhydro- β -D-glucopyranose), the pyrolysis product of cellulose, is a well-established marker for the combustion of biomass materials (Simoneit, 2002). Once partitioned into the particle phase, levoglucosan does not degrade, making it a useful tracer for long-range transport of biomass burning aerosol (Fraser and Lakshmanan, 2000). In total, 139 single particles were identified as having significant BBOA content (~ 5% of the particles).

The BBOA factor obtained from the average ensemble measurements shown in Figure 4-7 suggests that more than 5% of the nonrefractory aerosol mass could be contributed to biomass burning sources (the BBOA factor has yet to be established as a quantitative measure of biomass burning particulate matter). The number of detected single particles with significant BBOA content may have been suppressed relative to other accumulation mode particles because the markers for biomass burning are (1) potassium ions at m/z = 39, which are formed via a different ionziation process (i.e. surface ionization) and (2) levoglucosan markers at m/z = 60 and 73, which exhibited low S/N for smaller particles as discussed in Section 4.4.2. While the absolute magnitude of biomass burning sources may not be adequately represented in the current data set, our single particle measurements indicate that biomass burning was a relatively minor source for particluate matter at T1 during the sampling period under discussion.

The meteorological conditions and co-located measurements of biomass burning markers at T1 (*Stone et al.*, 2008) are consistent with lower BBOA concentrations during the period of single particle sampling. BBOA particles observed at T1 could have been produced by wildfires and/or urban biomass burning sources. During the period of single

particle sampling (March 27-30), the regional meteorology was characterized in the afternoon by increased cloudiness and precipitation over the central plateau (*Fast et al.,* 2007 and *de Foy et al.,* 2008). As a result, the intensity and number of wildfires influencing the area were significantly lower than the previous three weeks (See Figure 14b in *Fast et al.,* 2007). Stone et al. (2008) measured average levoglucosan concentrations from March 18-22 and March 23-30 at the T1 site. During the earlier time period the levoglucosan concentration was found to be 217 ng/m³ while in the later time period (coinciding with our single particle sampling) the concentration decreased to 55 ng/m³.

The 139 single particles with significant BBOA composition were not included in the HOA and OOA analysis. With these particles removed, the reconstructed organic (HOA + OOA) accounted for 93% ($R^2 = 0.84$) of the measured single particle organic mass, suggesting that HOA and OOA give a reasonable, but not complete, description of the organics at T1. Since the BBOA SP filter removed organic particles with significant BBOA character, it is possible that some BBOA organic mass remains within the internally mixed single particles detected. This would prevent the HOA and OOA deconvolution technique from describing 100% of the of measured organic mass.

4.5.3.2 Inorganics

Single particle measurements of ammonium with the AMS were subject to high noise due to interference from background water vapor within the AMS chamber. Despite this challenge, ammonium was measured with reasonable accuracy for single particles with large amounts of ammonium nitrate, sulfate, and/or chloride (~50 % by mass). For smaller levels, the NH4 content of the single particles can be systematically

underestimated. As a result, in most cases the uncertainty in NH4 is the largest source of scatter in the calculation of the single particle mass fractions. Full neutralization of inorganic species has been previously observed during the dry season in the MCMA (Moya et al., 2003). The ensemble average measurements at T1 indicate that the inorganics present were fully neutralized. Based on this observation and on mass balance, we will assume that the inorganics were in the form of NH4NO3, (NH4)2SO4, and NH4Cl. The NH4 content of each single particle is therefore calculated from the measured single particle mass of nitrate, sulfate, and chloride, unless otherwise stated.

4.5.4 Mixing State of the Ambient Aerosol

The fractional compositions of all single particles measured during the 75 hours of sampling are plotted in Figure 4-8. The data are presented in five panels showing the mass fraction of HOA, OOA, NH₄NO₃, (NH₄)₂SO₄, and NH₄Cl for each particle, plotted as a function of the local sampling time. Each panel shows the measured single particle mass fraction of the designated chemical component. That is, every particle is plotted in each panel. The solid black trace plotted in each panel is the 30 minute average of the corresponding single particle mass fraction. The vertical black lines denote midnight on each of the sample days.



Figure 4-9. Time series of NH_4Cl , $(NH_4)_2SO_4$, NH_4NO_3 , OOA, and HOA single particle mass fractions. Data points are colored by HOA mass fraction as indicated in the upper left.

The majority of the single particles sampled at T1 were internal mixtures of more than one chemical component. This is evident from the lack of substantial numbers of particles in Figure 4-9 with mass fractions of any single component equal to 1. This observation is important as it provides insights into the rate of atmospheric processing of particles in the Mexico City basin and has implications for better understanding the ultimate fate and atmospheric effects of primary particles. The single particle data directly confirm assumptions that are typically drawn from ambient, ensemble sampling of size-resolved aerosol chemistry where the average chemical compositions of particles appear to be relatively constant as a function of particle size (*Salcedo et al.*, 2006). This observation also has implications for the classification of single particles by single particle techniques.

For example, Figure 4-9 shows that most of the ambient particles measured at T1 contained ammonium nitrate. The range of single particle NH_4NO_3 mass fractions was ~ 0.2-0.3 throughout the day and nighttime periods with the exception of higher NH_4NO_3 fractions observed in the late morning. This observation is strongly supported by the single particle mass spectra reported by Moffet et al. (2008a) for ATOFMS results obtained at the T0 site. Nearly all classified single particle types reported exhibit both NO₂ and NO₃ ions (see Figure 2 in *Moffet et al.*, 2008a). A slightly larger mass fraction range is observed for the OOA and $(NH_4)_2SO_4$ content of the single particles compared to the NH_4NO_3 content. Due to limited signal-to-noise levels in this preliminary version of the LS-ToF-AMS, we will not attempt to interpret whether the observed range in chemical compositions is real or artifact. Instead, we will focus on (1) the atmospheric processes that are apparent from the changing chemical compositions of single particles as a function of time of day and (2) the externally mixed particles that are apparent as their chemical compositions lie outside of this rather narrow range of internally mixed particles.

Figure 4-9 shows that the chemical compositions (highlighted by the 30 minute averages) of ambient particles were dominated by different chemical components

throughout the day. During the morning (~ 1 hour after sunrise), the NH₄NO₃ fraction of all single particles rapidly increased, peaking between 10:00-11:00 LT before rapidly declining in the early afternoon; The OOA mass fraction of the single particles increased gradually during the daylight hours, reaching a peak in the middle of the afternoon. The single particle (NH₄)₂SO₄ fractions were highest during the evening and overnight and included one instance of a peak in (NH₄)₂SO₄ during a strong plume event. In addition to these internally mixed chemical compositional changes, Figure 4-9 also shows evidence for externally mixed single particle chloride events occurring between 00:00-10:00 LT each day.

The most obvious exception to the observed internal mixing (in addition to the chloride particles) is the subset of single particles in Figure 4-9 with high HOA mass fractions. These particles were observed in highest number concentrations each day during the early morning rush hour with a secondary peak in number concentration apparent during the late evenings. The HOA component measured by the AMS has been shown to be correlated with primary emissions (*Zhang et al.*, 2005b; *Canagaratna et al.*, 2007). Ensemble HOA data at T1, obtained while operating the instrument in MS-Mode, show that the HOA factor was strongly correlated with measurements of CO and elemental carbon (EC). In agreement with our observations, the results from Moffet et al., (2008a) indicate that the only class of particles observed by the ATOFMS that did not contain nitrate was classified as 'EC' particles. The 'EC' particles observed at T0 were likely the same type of local, traffic-related combustion-generated particles as the HOA particles described here, as primary traffic-related particles typically contain black carbon

and hydrocarbon-like organic matter due to unburned lubricating oil, the major nonrefractory component of diesel emissions (Canagaratna et al., 2007; Sakurai et al., These correlations confirm that the ensemble HOA measurements were 2003). associated with primary emissions in Mexico City. In the case of single particles with significant HOA compositions, these particles can be classified as primary emission particles which were likely emitted into the atmosphere as HOA and EC containing particles and subsequently may have undergone atmospheric processing (gas-to-particle condensation or particle coagulation). An important aspect of urban air pollution is the processing and ultimate fate of primary emissions. A specific example is the fate of primary combustion particles that contain black carbon. With increased residence time in the atmosphere, black carbon particles are coated with secondary inorganic and organic condensates that dramatically change the optical, hygroscopic and CCN properties of the original particle (Bond et al., 2006; Ramanathan and Carmichael, 2008). The morphology and relative composition (i.e. black carbon core + unburnt lubricating oil) of combustion particles will depend on the condition of the engine as well as atmospheric variables such as temperature and pressure. Since Mexico City is located at a high altitude, combustion sources will burn more fuel-rich, resulting in elevated contributions from non-refractory chemical components in the emissions from vehicles. Thus, tracking particles with measurable HOA content provides a new method for classifying and characterizing primary, combustion-related particles and their subsequent atmospheric processing.

The color scheme for the points in all panels of Figure 4-9 was chosen with this in mind and indicates the HOA content of each particle. Thus, particles colored blue have high-HOA content, particles colored red have low-to-zero-HOA content, and particles colored purple (*i.e.* red+blue) have intermediate-HOA content with mass fractions. While the total number of measured particles was rather small in the current sample, Figure 4-9 explicitly shows that the high-HOA content particles were observed from ~ 20:00 to 9:00 LT every day. After 9:00 and before ~20:00 LT, the high-HOA particles were not measured, indicating that the 'fresh' HOA combustion particles were not observed during day-light hours. This observation is consistent with rapid photochemical activity coating the 'fresh' HOA particles during the day with photochemical products (or through particle coagulation). In the following section, we investigate the evolution of these primary particles' number, number fraction, and chemical composition as a function of the time-of-day.

4.5.4.1 Primary HOA particles and their processing

All of the single particles measured and analyzed were separated into the following categories in accord with the color scheme shown in Figure 4-9: (1) High-HOA - considered unprocessed primary particles, (2) Intermediate-HOA - considered processed primary particles, and (3) Low-HOA - considered accumulation particles, not definitively linked to primary (e.g. local combustion) sources. Figure 4-10 (lower panel) shows the number of single particles as a function of their HOA mass fraction and exhibits a bimodal distribution with a small mode peaking at HOA mass fraction of ~1.0 and a larger mode centered at HOA mass fraction ~0.05. Single particles with HOA mass fractions

equal to zero were not included in the figure or the subsequent analysis under the assumption that they were not primary, traffic-related particles. Figure 4-10 (upper panel) shows the average mass fractions of NH₄NO₃, (NH₄)₂SO₄, NH₄Cl and OOA. The NH₄Cl content remained low, less than 0.10 across the full range of HOA mass fractions reflecting the relatively minor contribution of this compound to the total primary particle chemical composition and mass. On the other hand, the average NH₄NO₃, (NH₄)₂SO₄, and OOA content of the particles increased with decreasing HOA mass fraction implying that these species did influence the primary particle composition.



Figure 4-10. Particle counts (lower panel) and average single particle composition (upper panel) as a function of HOA mass fraction.

Combining the information in the top and bottom of Figure 4-10 and the uncertainty measurements from Section 4.4.1.1, the 'fresh' HOA, combustion-generated particles are defined as particles with mass fractions greater than ~0.90 HOA. The larger mode at low HOA mass fractions represents HOA particles that have undergone significant atmospheric processing (i.e. internally mixed accumulation mode particles). Due to the limited number of total single particles sampled, we have chosen to characterize the processing of 'fresh' HOA particles by tracking the number and chemical composition of primary particles with HOA mass fractions between 0.10-0.90. This chosen range may contain particles influenced by more regional (i.e. slower) atmospheric processing, complicating our interpretation of localized processing of primary particles with time frames from minutes to hours.



Figure 4-11. Time trends in the (a) measured number and (b) number fraction of high-HOA, intermediate-HOA, and low-to-zero-HOA particles.

The diurnal trends of the number of high-HOA, intermediate-HOA and low-HOA particles are displayed in Figure 4-11a as a stacked plot. The number of particles in all categories decreased between 11:00-13:00 LT due to dilution caused by the rising boundary layer. The single particle data show that the numbers of high-HOA and intermediate-HOA particles were largest in the early morning (4:30-7:30 LT). The single particle data explicitly show that the number of high-HOA particles decreased to zero during the late morning while the number of intermediate-HOA particles remained relatively constant. As mentioned previously, the high-HOA particles originate from local combustion sources and build up in the atmosphere during the early morning hours. This is consistent with the meteorological conditions: low boundary layer (inhibiting

dilution of local emissions) and low photochemical activity (i.e. low production of secondary condensable species). The disappearance of high-HOA particles in the late morning (while the boundary layer was still relatively low, but after the sun had risen) suggests that the high-HOA particles were coated with secondary nitrate. This description of primary particle processing is not possible with ensemble HOA data alone and is consistent with ATOFMS measurements at the T0 site that show secondary nitrate species on traffic particles between 9:00-15:00 while pure traffic (EC) particles are detected prior to 9:00 (See Figure 8 in *Moffet et al.*, 2008a). Rapid processing of primary particles in the MCMA has also been reported from single particle microscopy methods (*Johnson et al.*, 2005; *Adachi and Buseck*, 2008).

To illustrate the connection between primary, HOA single particles and ensemble HOA measurements, we include the diurnal trend for ensemble HOA mass as the dashed grey line in Figure 4-11a (μ g/m³ plotted on the right-hand axis). The sum of the high-HOA and intermediate-HOA single particles follows a diurnal trend that is similar to ensemble HOA data. The fact that the HOA factor in the ensemble data has a similar trend and does not go to zero, as does the 'fresh' HOA single particles, supports the claim that the primary, HOA single particles and the ensemble HOA factors are related.

To quantify the mixing state of the ambient ensemble, the data in Figure 4-11a are re-plotted in Figure 4-11b in terms of the number fraction of each particle type. The data show that during the early morning rush hour \sim 30-40% of the particles are high-HOA or intermediate-HOA (light and dark blue traces). Prior to sunrise, \sim 10% of the particles are high-HOA. Once the sun has risen (\sim 9:00 LT), the high-HOA particles disappear while

~20% of the particles remain as intermediate-HOA (coated or processed HOA). During the evening rush hour, a second peak in the fraction of intermediate-HOA particles is observed comprising ~25% of the particles. After the sun has gone down (~20:00), the high-HOA particles reappear making up 5-10% of the particles. The majority (70-80%) of the particles detected are classified as low-to-zero-HOA particles, characteristic of internally mixed (e.g. processed) accumulation mode particles.

4.5.4.2 Influence of atmospheric processing on particle composition

To track the chemical transformations of the single particles as a function of the time-of-day we show the number fraction of particles containing NH₄NO₃, (NH₄)₂SO₄, NH₄Cl, and OOA in Figures 4-12a and 4-12b. Figure 4-12a displays the diurnal trends for intermediate-HOA particles while Figure 4-12b shows the diurnal trends for the low-to-zero-HOA particles. Particles with component mass fractions greater than 0.10 are counted as particles that contain that chemical component.


Figure 4-12. Time trends in the number (upper panel) and number fraction of 'coated' particles for (a) intermediate-HOA particles and (b) low-to-zero-HOA particles.

The upper panel of Figures 4-12a and b is a replot of the data in Figure 4-11a. The solid line shows the total number of intermediate-HOA particles (a) or low-to-zero-HOA particles (b). The broken line (same in both Figures a and b) is the number of high-HOA particles plotted with respect to the right-hand axis. This plot is presented to remind the reader that the high-HOA particles disappeared in the late morning after ~9:00 LT.

With the onset of photochemical activity (9:00-12:00 LT), the number of intermediate-HOA particles that contain NH4NO3 increases from 80% to 100%. Likewise, an increase from 95% to 100% of the low-to-zero-HOA particles that contain NH_4NO_3 is observed between 9:00-12:00 LT. The fact that all single particles measured between 9:00-12:00 LT contained NH_4NO_3 suggests rapid condensation of secondary nitrate onto all pre-exisiting particles. Given the distance of likely high-HOA particle source from T1 (the highway ~ 1 km away) and the average wind speed and direction, we calculate that the primary HOA particles were coated with NH₄NO₃ in ~15-30 minutes during this time period. We note that the fraction of intermediate-HOA particles containing NH4NO3 decreased back to ~80% after 12:00. The rise and fall in fraction of particles with ntirate was due to the temperature-dependent equilibrium constant in the reaction: $NH_{3 (g)} + HNO_{3 (g)} \leftrightarrow NH_4NO_{3 (s)}$. The MCMA atmosphere contains high concentrations of gas phase NH3. Nitric acid is formed from reaction of NO2 and photochemically-produced OH radicals. Therefore, with sufficient sunlight to produce OH radicals, HNO₃ will be form in a single oxidation step. In the early morning at T1, the temperature was low, resulting in conversion of the HNO₃ to NH₄NO₃ which subsequently condensed onto all pre-existing particles. As the temperature increased in the late morning and early afternoon, the dissociation of NH₄NO₃ back to NH₃ and HNO₃ was favored. These results are consistent with the results of Zheng et al. (2008) who monitored the particulate NO₃ and gas phase HNO₃ concentrations at T0.

During the afternoon hours, the number of intermediate-HOA particles infuenced by OOA steadily increases from ~ 30% (prior to 12:00) to ~ 55% (12:00-15:00 LT) to ~

73% (15:00-18:00 LT). For the low-to-zero-HOA particles, ~ 90% of the particles contained OOA in the morning and 100% contained OOA in the afternoon. Rapid formation of secondary organic aerosol in the MCMA region has been previously reported (*Volkamer et al.*, 2006). The single particle data presented here indicate that OOA condenses onto nearly all single particles measured between 15:00-18:00 LT. Unlike the secondary nitrate, secondary organic species typically require multiple oxidation steps prior to forming oxygenated organic aerosol or condensing organic material on pre-existing particles (*Kroll and Seinfeld*, 2008). During the early morning time period when secondary nitrate formation dominates the single particle composition, the production rate of OOA is slower than in the mid afternoon (*Volkamer et al.*, 2006). The single partice data presented here suggest important temporal differences between secondary inorganic and organic processes that have implications for optical, hygroscopic, and CCN treatments of primary particle processing in urban environments.

Particles that contain $(NH_4)_2SO_4$ were most prevalent during the evening and overnight time periods (18:00-24:00 LT). For the intermediate-HOA particles, ~ 65% of the particles contained $(NH_4)_2SO_4$ in the late evening and overnight compared to ~36% during the middle of the day. A similar increase was observed for the low-to-zero-HOA particles from ~ 69% during the middle of the day to ~ 93% in the evening and overnight. Sulfate has been reported to be a major component of PM_{2.5} in the MCMA (*Salcedo et al.*, 2006; *Johnson et al.*, 2005; *Johnson et al.*, 2006; *Querol et al.*, 2008; *DeCarlo et al.*, 2008; *Kleinman et al.*, 2008). The major formation pathway of particulate sulfate is aqueous phase SO₂ oxidation (*Salcedo et al.*, 2006). In the MCMA, SO₂ has significant anthropogenic (the Tula refinery complex and industrial regions concentrated in the northwest) and natural (the active Popocatepetl volcano in the southwest) sources. Given the general lack of spatial variability in sulfate concentrations, sulfate is typically attributed to regional-scale atmospheric processing (*Querol et al.*, 2008; *DeCarlo et al.*, 2008). The single particle observations of a broad range of measured (NH₄)₂SO₄ mass fractions and diurnal pattern that peaked in the late evening and overnight are consistent with regional-scale production and accumulation of particulate sulfate. A detailed examination of the single particle (NH₄)₂SO₄ content during a SO₂ plume event at T1 is provided in Section 4.5.4.3.

The fraction of particles containing NH₄Cl was highest for intermediate-HOA and low-to-zero-HOA particles during the early morning hours (00:00-10:00 LT). At this time, ~15-20% of the intermediate-HOA particles and ~30-40% of the low-to-zero-HOA particles contained NH₄Cl. Since the fraction of particles with NH₄Cl was highest during the overnight period it is unlikely that the chloride was formed via photochemical reactions. The lower fraction of particles influenced by chloride suggests that the chloride may have come from a unique source. A detailed discussion of the potential sources of the high chloride containing particles is provided in Section 4.5.4.4.

4.5.4.3 SO₂ plume event

Returning to Figure 4-9 we note that a brief period of high single particle (NH4)2SO4 was observed on March 28th at 19:00 LT. Back trajectories for the time period during high single particle (NH4)2SO4 indicate that the air was arriving at T1 directly from the northwest. The Tula power plant refinery complex is located \sim 50 km

to the northwest of T1 and has been shown to emit high concentrations of SO2 into the MCMA region (Johnson et al., 2006; Kleinman et al., 2008; DeCarlo et al., 2008; Fast et al., 2007, Querol et al., 2008). Co-located gas phase measurements at T1 confirmed that the plume measured at this time contained elevated levels of SO2 (~8 ppb). During the SO2 plume, 100% of the single particles measured at T1 had (NH4)2SO4 mass fractions of 0.60 or greater. The fact that all the particles measured at this time contained elevated levels of (NH4)2SO4 suggests that gas phase SO2 oxidation followed by gas-to-particle condensation or heterogeneous oxidation of SO2 to SO4 occurred within the SO2 plume as it was advected from Tula to the T1 site.

As the conversion from SO_2 to SO_4 is a slow gas phase process (*Seinfeld and Pandis*, 2006; *Stockwell and Calvert*, 1983) and its heterogeneous conversion is dependent upon particle chemical compositions, particulate sulfate is often associated with slower, regional-scale atmospheric processing, but this instance of high single particle sulfate was the result of point source emissions rather than regional-scale processing. Anthropogenic SO_2 emissions, such as the observed Tula plume, have direct effects on the processing or aging of all of the entrained particles and may provide a source for much of the increased sulfate mass fractions during the late evening and overnight time periods.

4.5.4.4 High chloride content single particles

A second feature in Figure 4-9 was the presence of a subset of single particles with high chloride content observed between 00:00-10:00 LT each day. During these times, ~ 10% of the total single particles sampled had NH4Cl mass fractions > 0.10. The

presence of these high chloride particles indicates that these externally mixed particles may have a specific, identifiable source.

During the MILAGRO study, Moffet el al. (2008a,b) used an ATOFMS located at the T0 site to measure the chemical composition of single particles. Results from the ATOFMS show that a large fraction of the total particles sampled between 2:00-5:00 LT each morning were internally mixed Pb-Zn-Cl particles (*Moffet et al.*, 2008b). Given this mixed composition, and the spatial and temporal distribution of PbZnCl particles, Moffet concluded that the early morning chloride particles originated at industrial sites located in the northern region of the city. In addition to industrial sources, potential sources of chloride in the MCMA region include emissions from biomass and trash burning, drinking water, and waste-water treatment facilities (*Tanaka et al.*, 2003).

The single particle measurements made with the LS-ToF-AMS are not chemically sensitive to heavy metal species such as Zn and Pb because the time scale for vaporization of such species is longer than the 6 ms PTOF saving interval. On the other hand, ensemble measurements in MS mode can be examined over longer time scales (minutes) and can help determine if heavy metals are present in the aerosol particles. Close examination of the ensemble data acquired during time periods of high chloride signal indicate that Pb was present in about half of the instances of high particulate chloride. In such cases, the Pb signal was approximately 100 times smaller than the chloride signal. Care must be taken when interpreting AMS measurements of heavy metals and further characterization of the ionization efficiency of metal species must be done before quantitative information is reported. Nevertheless, on a qualitative basis, these observations suggest that only some of the chloride events at T1 were correlated

with Pb, and that when present, lead constituted a relatively minor component of the total particle mass. Lower concentrations of Pb containing particles were also measured at the T1 site relative to the T0 site by Moreno et al., (2008).

Although the single particle detection is not chemically sensitive to metal species, the size information obtained with the LS-ToF-AMS can be used to gain additional insight into the presence of heavy metals in the single particles. The densities of PbCl₂ and ZnCl₂ are 5.85 g/cm³ and 2.90 g/cm³ respectively. If a single particle were predominately composed of these species it would have a significantly higher density than the majority of other submicron ambient aerosol particles (typically $\rho = 0.9 - 1.8$ g/cm³). The simultaneous measure of d_{va} and d_o provides a per particle measure of the effective density of all single particles, independent of chemical detection. Examination of all single particles measured during the high chloride particle events show that no particles had effective densities greater than 1.8 g/cm³. This evidence suggests that if PbCl₂ and ZnCl₂ were present in the particles, it comprised a relatively minor amount of the total single particle mass. Our results are consistent with the observations of *Murphy* et al., (2007b) who studied the Pb content of single particles throughout the United States with the PALMS, ATOFMS, and RSMS single particle mass spectrometers. Murphy emphasizes the importance of understanding the chemical detection sensitivity of single particle mass spectrometers. Calibration experiments indicate that the PALMS and ATOFMS instruments are ~ 12 times more sensitive to metal species than detection of NH_4NO_3 or HNO_3 . Therefore, when measuring single particles with any Pb content, it is

possible to over-estimate the mass contribution of the metal species to the total particle composition with laser-ablation single particle mass spectrometers.

Our single particle measurements at T1 suggest that the predominant form of chloride in the single particles was ammonium chloride. This is consistent with the meteorological conditions. During the early morning, when the high chloride particles were observed, the temperature was low and the relative humidity was high, conditions that favor the formation and condensation of more volatile ammonium chloride from reaction of $HCl_{(g)}$ and $NH_{3(g)}$ (*San Martini et al.*, 2006a; *San Martini et al.*, 2006b; *Salcedo et al.*, 2006).



Figure 4-13. (a) Measured (i.e. real) single particle NH_4 mass plotted versus calculated single particle NH_4 mass for the subset of single particles with high chloride content. (b) Single particle mass spectrum for a typical high chloride content particle (identified in (a) with the arrow).

Further, a mass balance examination of the NH₄ content of the high chloride particles is consistent with the composition of the particles being NH₄Cl. The identification of the chloride component as NH₄Cl is supported by the data displayed in Figure 4-13a. This figure plots the 'real' NH₄ mass, measured by the mass spectrometer as a function of the amount of calculated NH₄ required to fully neutralize the per particle inorganic content (i.e. neutralized to (NH₄)₂SO₄, NH₄NO₃, and NH₄Cl). The correlation is reasonable ($R^2 = 0.75$; slope = 0.95). The particles displayed in Figure 4-13a have NH₄Cl mass fractions of 0.40 or greater and most were internally mixed with NH₄NO₃. The NH₄NO₃ mass fraction of each particle is indicated by the color of the data points as indicated in the legend. In Figure 4-13b we show the mass spectrum for the single particle denoted with an arrow in Figure 4-13a. The mass spectrum shows that this particle was predominately NH₄Cl combined with some NH₄NO₃ and very little organic. Based on these observations, we conclude that a significant fraction of the particulate chloride measured with the LS-ToF-AMS at T1 was in the form of NH₄Cl.

4.6 SUMMARY

This chapter reported the first single particle results obtained with the Aerodyne time-of-flight aerosol mass spectrometer equipped with a light scattering module (LS-ToF-AMS). The LS-ToF-AMS was deployed during the MILAGRO 2006 campaign at the T1 ground site ~ 40 km northeast of Mexico City. With the LS-ToF-AMS single particle and ensemble average aerosol properties were measured from the same operating platform. While operating in the single particle mode, 12,853 optically-triggered single particle mass spectra were saved and analyzed during 75 hours of continuous sampling.

Analysis of the mass composition of the single particles allowed the LS-ToF-AMS to provide insights about the mixing state, source contributions and chemical transformations of the ambient aerosol particles in the MCMA. The following results were obtained in this study:

1. Using the single particle detection capabilities of this instrument, the detection efficiency of the AMS was quantitatively determined.

2. Based on the time required for the particles to be vaporized, ionized and detected, particles were categorized into three types: prompt vaporization, delayed vaporization, and 'null' vaporization. Null particles are those detected optically but do not produce a measurable chemical ion signal. Prompt particles made up 23% of the total number and 59% of the total mass. Delayed particles made up 26% of the total number and 38% of the total mass. Null particles made up 51% of the total number and 3% of the total mass. The study shows that the mass content of particles undergoing prompt vaporization is reliably measured. Detailed analysis was preformed for this class of particles.

3. The single particle mass measurement was shown to be in quantitative agreement with average ensemble mass measurements.

4. The single particle mass components were categorized into HOA, OOA, NH₄NO₃, (NH₄)₂SO₄, and NH₄Cl fractions and were displayed as a function of sampling time.

5. The measurement of chemical composition allowed the identification of time periods during which the ambient ensemble was externally mixed. In some cases the chemical composition of the particles suggested a likely source.

6. During morning rush hour (4:00-9:00 LT) each day the ambient ensemble was an external mixture of combustion-generated unprocessed HOA particles from local traffic and other particles of mixed composition.

7. From 9:00-12:00 LT all particles within the ambient ensemble, including HOA particles originating from local traffic sources, were coated with NH_4NO_3 due to photochemical production HNO₃. NH_4NO_3 condensation was more rapid than OOA condensation during the late morning hours.

9. During the afternoon hours (12:00-18:00 LT), OOA condensation occurred, causing an increase in the average single particle OOA mass fraction of the majority of the single particles.

10. During a single time period, gas-to-particle condensation of $(NH_4)_2SO_4$ was observed within a strong SO_{2 (g)} plume arriving at T1 from the northwest.

11. Particles with high NH₄Cl mass fractions were identified during early morning periods.

12. Particles with mass spectral features characterized by biomass burning were also identified.

4.7 REFERENCES FOR CHAPTER IV

Adachi, K. & Buseck, P.R. 2008, "Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City", *Atmospheric Chemistry and Physics Discussions*, vol. 8, no. 3, pp. 9179-9207.

- Alfarra, M.R. 2004, *Insights into atmospheric organic aerosols using an aerosol mass spectrometer*, University of Manchester.
- Alfarra, M.R., Prevot, A.S.H., Szidat, S., Sandradewi, J., Weimer, S., Lanz, V.A., Schreiber, D., Mohr, M. & Baltensperger, U. 2007, "Identification of the mass spectral signature of organic aerosols from wood burning emissions", *Environmental science & technology*, vol. 41, no. 16, pp. 5770-5777.
- Allan, J.D., Delia, A.E., Coe, H., Bower, K.N., Alfarra, M.R., Jimenez, J.L., Middlebrook, A.M., Drewnick, F., Onasch, T.B., Canagaratna, M.R., Jayne, J.T. & Worsnopf, D.R. 2004, "A generalised method for the extraction of chemically resolved mass spectra from aerodyne aerosol mass spectrometer data", *Journal of Aerosol Science*, vol. 35, no. 7, pp. 909-922.
- Bahreini, R., Jimenez, J.L., Wang, J., Flagan, R.C., Seinfeld, J.H., Jayne, J.T. & Worsnop, D.R. 2003, "Aircraft-based aerosol size and composition measurements during ACE-Asia using an Aerodyne aerosol mass spectrometer", *Journal of Geophysical Research-Atmospheres*, vol. 108, no. D23.
- Barnard, J.C., Kassianov, E.I., Ackerman, T.P., Johnson, K., Zuberi, B., Molina, L.T. & Molina, M.J. 2007, "Estimation of a "radiatively correct" black carbon specific absorption during the Mexico City Metropolitan Area (MCMA) 2003 field campaign", *Atmospheric Chemistry and Physics*, vol. 7, no. 6, pp. 1645-1655.
- Baynard, T., Garland, R.M., Ravishankara, A.R., Tolbert, M.A. & Lovejoy, E.R. 2006, "Key factors influencing the relative humidity dependence of aerosol light scattering", *Geophysical Research Letters*, vol. 33, no. 6.
- Bond, T.C. & Bergstrom, R.W. 2006, "Light absorption by carbonaceous particles: An investigative review", *Aerosol Science and Technology*, vol. 40, no. 1, pp. 27-67.
- Canagaratna, M.R., Jayne, J.T., Ghertner, D.A., Herndon, S., Shi, Q., Jimenez, J.L., Silva, P.J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K.L., Kolb, C.E. & Worsnop, D.R. 2004, "Chase studies of particulate emissions from in-use New York City vehicles", *Aerosol Science and Technology*, vol. 38, no. 6, pp. 555-573.
- Canagaratna, M.R., Jayne, J.T., Jimenez, J.L., Allan, J.D., Alfarra, M.R., Zhang, Q., Onasch, T.B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L.R., Trimborn, A.M., Northway, M.J., DeCarlo, P.F., Kolb, C.E., Davidovits, P. &

Worsnop, D.R. 2007, "Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer", *Mass spectrometry reviews*, vol. 26, no. 2, pp. 185-222.

- Chylek, P., Videen, G., Ngo, D., Pinnick, R.G. & Klett, J.D. 1995, "Effect of black carbon on the optical properties and climate forcing of sulfate aerosols", *Journal of Geophysical Research-Atmospheres*, vol. 100, no. D8, pp. 16325-16332.
- Cross, E.S., Slowik, J.G., Davidovits, P., Allan, J.D., Worsnop, D.R., Jayne, J.T., Lewis, D.K., Canagaratna, M. & Onasch, T.B. 2007, "Laboratory and ambient particle density determinations using light scattering in conjunction with aerosol mass spectrometry", *Aerosol Science and Technology*, vol. 41, no. 4, pp. 343-359.
- de Foy, B., Fast, J.D., Paech, S.J., Phillips, D., Walters, J.T., Coulter, R.L., Martin, T.J., Pekour, M.S., Shaw, W.J., Kastendeuch, P.P., Marley, N.A., Retama, A. & Molina, L.T. 2008, "Basin-scale wind transport during the MILAGRO field campaign and comparison to climatology using cluster analysis", *Atmospheric Chemistry and Physics*, vol. 8, no. 5, pp. 1209-1224.
- DeCarlo, P.F., Dunlea, E.J., Kimmel, J.R., Aiken, A.C., Sueper, D., Crounse, J., Wennberg, P.O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D.R., Knapp, D., Weinheimer, A.J., Montzka, D.D., Campos, T. & Jimenez, J.L. 2008, "Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign", *Atmospheric Chemistry and Physics*, vol. 8, no. 14, pp. 4027-4048.
- DeCarlo, P.F., Kimmel, J.R., Trimborn, A., Northway, M.J., Jayne, J.T., Aiken, A.C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K.S., Worsnop, D.R. & Jimenez, J.L. 2006, "Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer", *Analytical Chemistry*, vol. 78, no. 24, pp. 8281-8289.
- Doran, J.C., Barnard, J.C., Arnott, W.P., Cary, R., Coulter, R., Fast, J.D., Kassianov, E.I., Kleinman, L., Laulainen, N.S., Martin, T., Paredes-Miranda, G., Pekour, M.S., Shaw, W.J., Smith, D.F., Springston, S.R. & Yu, X.Y. 2007, "The T1-T2 study: evolution of aerosol properties downwind of Mexico City", *Atmospheric Chemistry* and Physics, vol. 7, no. 6, pp. 1585-1598.
- Drewnick, F., Hings, S.S., DeCarlo, P., Jayne, J.T., Gonin, M., Fuhrer, K., Weimer, S., Jimenez, J.L., Demerjian, K.L., Borrmann, S. & Worsnop, D.R. 2005, "A new time-

of-flight aerosol mass spectrometer (TOF-AMS) - Instrument description and first field deployment", *Aerosol Science and Technology*, vol. 39, no. 7, pp. 637-658.

- Drewnick, F., Schwab, J.J., Jayne, J.T., Canagaratna, M., Worsnop, D.R. & Demerjian, K.L. 2004, "Measurement of ambient aerosol composition during the PMTACS-NY 2001 using an aerosol mass spectrometer. Part I: Mass concentrations", *Aerosol Science and Technology*, vol. 38, pp. 92-103.
- Fast, J.D., de Foy, B., Rosas, F.A., Caetano, E., Carmichael, G., Emmons, L., McKenna, D., Mena, M., Skamarock, W., Tie, X., Coulter, R.L., Barnard, J.C., Wiedinmyer, C. & Madronich, S. 2007, "A meteorological overview of the MILAGRO field campaigns", *Atmospheric Chemistry and Physics*, vol. 7, no. 9, pp. 2233-2257.
- Fraser, M.P. & Lakshmanan, K. 2000, "Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols", *Environmental science & technology*, vol. 34, no. 21, pp. 4560-4564.
- Fuller, K.A., Malm, W.C. & Kreidenweis, S.M. 1999, "Effects of mixing on extinction by carbonaceous particles", *Journal of Geophysical Research-Atmospheres*, vol. 104, no. D13, pp. 15941-15954.
- Gard, E., Mayer, J.E., Morrical, B.D., Dienes, T., Fergenson, D.P. & Prather, K.A. 1997, "Real-time analysis of individual atmospheric aerosol particles: Design and performance of a portable ATOFMS", *Analytical Chemistry*, vol. 69, no. 20, pp. 4083-4091.
- Herndon, S. C., Timothy B. Onasch, Ezra C. Wood, Jesse H. Kroll, Manjula R. Canagaratna, John T. Jayne, Miguel A. Zavala, W. Berk Knighton, Claudio Mazzoleni, Manvendra K. Dubey, Ingrid M. Ulbrich, Jose L. Jimenez Robert Seila, Joost A. de Gouw, Benjamin de Foy, Jerome Fast, Luisa T. Molina, Charles E.Kolb and Douglas R.Worsnop 2008, "The correlation of secondary organic aerosol with odd oxygen in Mexico City", *Journal of Geophysical Research*, .
- Hogrefe, O., Schwab, J.J., Drewnick, F., Lala, G.G., Peters, S., Demerjian, K.L., Rhoads, K., Felton, H.D., Rattigan, O.V., Husain, L. & Dutkiewicz, V.A. 2004, "Semicontinuous PM2.5 sulfate and nitrate measurements at an urban and a rural location in New York: PMTACS-NY summer 2001 and 2002 campaigns", pp. 1040.

- Huffman, J.A., Jayne, J.T., Drewnick, F., Aiken, A.C., Onasch, T., Worsnop, D.R. & Jimenez, J.L. 2005, "Design, modeling, optimization, and experimental tests of a particle beam width probe for the aerodyne aerosol mass spectrometer", *Aerosol Science and Technology*, vol. 39, no. 12, pp. 1143-1163.
- Jayne, J.T., Leard, D.C., Zhang, X.F., Davidovits, P., Smith, K.A., Kolb, C.E. & Worsnop, D.R. 2000, "Development of an aerosol mass spectrometer for size and composition analysis of submicron particles", *Aerosol Science and Technology*, vol. 33, no. 1-2, pp. 49-70.
- Jimenez, J.L., Jayne, J.T., Shi, Q., Kolb, C.E., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., Zhang, X.F., Smith, K.A., Morris, J.W. & Davidovits, P. 2003, "Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer", *Journal of Geophysical Research-Atmospheres*, vol. 108, no. D7.
- Johnson, K.S., de Foy, B., Zuberi, B., Molina, L.T., Molina, M.J., Xie, Y., Laskin, A. & and Shutthanandan, V. 2006, "Aerosol composition and source apportionment in the Mexico City Metropolitan Area with PIXE/PESA/STIM and multivariate analysis", *Atmos. Chem. Phys.*, vol. 6, pp. 4591-4600.
- Johnson, K.S., de Foy, B., Zuberi, B., Molina, L.T., Molina, M.J., Xie, Y., Laskin, A. & Shutthanandan, V. 2006, "Aerosol composition and source apportionment in the Mexico City Metropolitan Area with PIXE/PESA/STIM and multivariate analysis", *Atmospheric Chemistry and Physics*, vol. 6, pp. 4591-4600.
- Johnson, K.S., Zuberi, B., Molina, L.T., Molina, M.J., Iedema, M.J., Cowin, J.P., Gaspar, D.J., Wang, C. & Laskin, A. 2005, "Processing of soot in an urban environment: case study from the Mexico City Metropolitan Area", *Atmospheric Chemistry and Physics*, vol. 5, pp. 3033-3043.
- Kleinman, L.I., Springston, S.R., Daum, P.H., Lee, Y.N., Nunnermacker, L.J., Senum, G.I., Wang, J., Weinstein-Lloyd, J., Alexander, M.L., Hubbe, J., Ortega, J., Canagaratna, M.R. & Jayne, J. 2008, "The time evolution of aerosol composition over the Mexico City plateau", *Atmospheric Chemistry and Physics*, vol. 8, no. 6, pp. 1559-1575.
- Kroll, J.H. & Seinfeld, J.H. 2008, "Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere", *Atmospheric Environment*, vol. 42, no. 16, pp. 3593-3624.

- Lanz, V.A., Alfarra, M.R., Baltensperger, U., Buchmann, B., Hueglin, C. & Prevot, A.S.H. 2007, "Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra", *Atmospheric Chemistry and Physics*, vol. 7, no. 6, pp. 1503-1522.
- Lanz, V.A., Alfarra, M.R., Baltensperger, U., Buchmann, B., Hueglin, C., Szidat, S., Wehrli, M.N., Wacker, L., Weimer, S., Caseiro, A., Puxbaum, H. & Prevot, A.S.H. 2008, "Source attribution of submicron organic aerosols during wintertime inversions by advanced factor analysis of aerosol mass spectra", *Environmental science & technology*, vol. 42, no. 1, pp. 214-220.
- Lesins, G., P. Chylek, and U.Lohmann 2002, "A study of internal and external mixing scenarios and its effect on aerosol optical properties and direct radiative forcing", *J.Geophys.Res.*, 110, D07S09, vol. 107(D10), pp. 4094.
- Liu, P.S.K., Deng, R., Smith, K.A., Williams, L.R., Jayne, J.T., Canagaratna, M.R., Moore, K., Onasch, T.B., Worsnop, D.R. & Deshler, T. 2007, "Transmission efficiency of an aerodynamic focusing lens system: Comparison of model calculations and laboratory measurements for the Aerodyne Aerosol Mass Spectrometer", *Aerosol Science and Technology*, vol. 41, no. 8, pp. 721-733.
- McMurry, P.H. 2000, "A review of atmospheric aerosol measurements", *Atmospheric Environment*, vol. 34, no. 12-14, pp. 1959-1999.
- Moffet, R.C., de Foy, B., Molina, L.T., Molina, M.J. & Prather, K.A. 2008, "Measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry", *Atmospheric Chemistry and Physics*, vol. 8, no. 16, pp. 4499-4516.
- Moffet, R.C., Qin, X.Y., Rebotier, T., Furutani, H. & Prather, K.A. 2008, "Chemically segregated optical and microphysical properties of ambient aerosols measured in a single-particle mass spectrometer", *Journal of Geophysical Research-Atmospheres*, vol. 113, no. D12.
- Moffet, R.C., Desyaterik, Y., Hopkins, R.J., Tivanski, A.V., Gilles, M.K., Wang, Y., Shuthanandan, V., Molina, L.T., Abraham, R.G., Johnson, K.S., Mugica, V., Molina, M.J., Laskin, A. & Prather, K.A. 2008, "Characterization of Aerosols Containing Zn, Pb, and Cl from an Industrial Region of Mexico City", *Environ.Sci.Technol.*, vol. 42, no. 19, pp. 7091-7097.

- Moreno, T., Querol, X., Pey, J., Minguillon, M.C., Perez, N., Alastuey, A., Bernabe, R.M., Blanco, S., Cardenas, B., Eichinger, W., Salcido, A. & Gibbons, W. 2008, "Spatial and temporal variations in inhalable CuZnPb aerosols within the Mexico City pollution plume", *Journal of Environmental Monitoring*, vol. 10, no. 3, pp. 370-378.
- Moya, M., Castro, T., Zepeda, M. & Baez, A. 2003, "Characterization of sizedifferentiated inorganic composition of aerosols in Mexico City", *Atmospheric Environment*, vol. 37, no. 25, pp. 3581-3591.
- Murphy, D.M. 2007, "The design of single particle laser mass spectrometers", *Mass spectrometry reviews*, vol. 26, no. 2, pp. 150-165.
- Murphy, D.M., Hudson, P.K., Cziczo, D.J., Gallavardin, S., Froyd, K.D., Johnston, M.V., Middlebrook, A.M., Reinard, M.S., Thomson, D.S., Thornberry, T. & Wexler, A.S. 2007, "Distribution of lead in single atmospheric particles", *Atmospheric Chemistry* and Physics, vol. 7, no. 12, pp. 3195-3210.
- Murphy, D.M., Middlebrook, A.M. & Warshawsky, M. 2003, "Cluster analysis of data from the Particle Analysis by Laser Mass Spectrometry (PALMS) instrument", *Aerosol Science and Technology*, vol. 37, no. 4, pp. 382-391.
- Murphy, D.M. & Thomson, D.S. 1995, "LASER IONIZATION MASS-SPECTROSCOPY OF SINGLE AEROSOL-PARTICLES", Aerosol Science and Technology, vol. 22, no. 3, pp. 237-249.
- Nash, D.G., T. Baer, M.V.Johnston 2006, "Aerosol mass spectrometry: An introductory review", *International Journal of Mass Spectrometry*, vol. 258, no. 1-3, pp. 2-12.
- Petters, M.D., Prenni, A.J., Kreidenweis, S.M., DeMott, P.J., Matsunaga, A., Lim, Y.B.
 & Ziemann, P.J. 2006, "Chemical aging and the hydrophobic-to-hydrophilic conversion of carbonaceous aerosol", *Geophysical Research Letters*, vol. 33, no. 24.
- Phares, D.J., Rhoads, K.P. & Wexler, A.S. 2002, "Performance of a single ultrafine particle mass spectrometer", *Aerosol Science and Technology*, vol. 36, no. 5, pp. 583-592.

- Phares, D.J., Rhoads, K.P., Wexler, A.S., Kane, D.B. & Johnston, M.V. 2001, "Application of the ART-2a algorithm to laser ablation aerosol mass spectrometry of particle standards", *Analytical Chemistry*, vol. 73, no. 10, pp. 2338-2344.
- Querol, X., Pey, J., Minguillon, M.C., Perez, N., Alastuey, A., Viana, M., Moreno, T., Bernabe, R.M., Blanco, S., Cardenas, B., Vega, E., Sosa, G., Escalona, S., Ruiz, H. & Artinano, B. 2008, "PM speciation and sources in Mexico during the MILAGRO-2006 Campaign", *Atmospheric Chemistry and Physics*, vol. 8, no. 1, pp. 111-128.
- Quinn, P.K. & Bates, T.S. 2005, "Regional aerosol properties: Comparisons of boundary layer measurements from ACE 1, ACE 2, aerosols99, INDOEX, ACE asia, TARFOX, and NEAQS", *Journal of Geophysical Research-Atmospheres*, vol. 110, no. D14.
- Ramanathan, V. & Carmichael, G. 2008, "Global and regional climate changes due to black carbon", *Nature Geoscience*, vol. 1, no. 4, pp. 221-227.
- Sakurai, H., Tobias, H.J., Park, K., Zarling, D., Docherty, S., Kittelson, D.B., McMurry, P.H. & Ziemann, P.J. 2003, "On-line measurements of diesel nanoparticle composition and volatility", *Atmospheric Environment*, vol. 37, no. 9-10, pp. 1199-1210.
- Salcedo, D., Onasch, T.B., Dzepina, K., Canagaratna, M.R., Zhang, Q., Huffman, J.A., DeCarlo, P.F., Jayne, J.T., Mortimer, P., Worsnop, D.R., Kolb, C.E., Johnson, K.S., Zuberi, B., Marr, L.C., Volkamer, R., Molina, L.T., Molina, M.J., Cardenas, B., Bernabe, R.M., Marquez, C., Gaffney, J.S., Marley, N.A., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Lesher, R., Shirley, T. & Jimenez, J.L. 2006, "Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite", *Atmospheric Chemistry and Physics*, vol. 6, pp. 925-946.
- San Martini, F.M., Dunlea, E.J., Grutter, M., Onasch, T.B., Jayne, J.T., Canagaratna, M.R., Worsnop, D.R., Kolb, C.E., Shorter, J.H., Herndon, S.C., Zahniser, M.S., Ortega, J.M., McRae, G.J., Molina, L.T. & Molina, M.J. 2006, "Implementation of a Markov Chain Monte Carlo method to inorganic aerosol modeling of observations from the MCMA-2003 campaign Part I: Model description and application to the La Merced site", *Atmospheric Chemistry and Physics*, vol. 6, pp. 4867-4888.

- San Martini, F.M., Dunlea, E.J., Volkamer, R., Onasch, T.B., Jayne, J.T., Canagaratna, M.R., Worsnop, D.R., Kolb, C.E., Shorter, J.H., Herndon, S.C., Zahniser, M.S., Salcedo, D., Dzepina, K., Jimenez, J.L., Ortega, J.M., Johnson, K.S., McRae, G.J., Molina, L.T. & Molina, M.J. 2006, "Implementation of a Markov Chain Monte Carlo method to inorganic aerosol modeling of observations from the MCMA-2003 campaign Part II: Model application to the CENICA, Pedregal and Santa Ana sites", *Atmospheric Chemistry and Physics*, vol. 6, pp. 4889-4904.
- Schneider, J., Weimer, S., Drewnick, F., Borrmann, S., Helas, G., Gwaze, P., Schmid, O., Andreae, M.O. & Kirchner, U. 2006, "Mass spectrometric analysis and aerodynamic properties of various types of combustion-related aerosol particles", *International Journal of Mass Spectrometry*, vol. 258, no. 1-3, pp. 37-49.
- Seinfeld, J.H., S.N.Pandis 2006, *Atmospheric Chemistry and Physics: From Air Pollution* to Climate Change, John Wiley & Sons, Inc., New York.
- Shilling, J.E., King, S.M., Mochida, M. & Martin, S.T. 2007, "Mass spectral evidence that small changes in composition caused by oxidative aging processes alter aerosol CCN properties", *Journal of Physical Chemistry A*, vol. 111, no. 17, pp. 3358-3368.
- Simoneit, B.R.T. 2002, "Biomass burning A review of organic tracers for smoke from incomplete combustion", *Applied Geochemistry*, vol. 17, no. 3, pp. 129-162.
- Solomon, S., Qin, D., Manning, M., Marquis, M., Averyt, K., Tignor, M. & and Miller, H.L.(. 2007, *IPCC: Climate change 2007: The Scientific Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Song, X.H., Hopke, P.K., Fergenson, D.P. & Prather, K.A. 1999, "Classification of single particles analyzed by ATOFMS using an artificial neural network, ART-2A", *Analytical Chemistry*, vol. 71, no. 4, pp. 860-865.
- Stockwell, W.R. & Calvert, J.G. 1983, "THE MECHANISM OF THE HO-SO2 REACTION", *Atmospheric Environment*, vol. 17, no. 11, pp. 2231-2235.
- Stone, E.A., Snyder, D.C., Sheesley, R.J., Sullivan, A.P., Weber, R.J. & Schauer, J.J. 2008, "Source apportionment of fine organic aerosol in Mexico City during the

MILAGRO experiment 2006", *Atmospheric Chemistry and Physics*, vol. 8, no. 5, pp. 1249-1259.

- Su, Y.X., Sipin, M.F., Furutani, H. & Prather, K.A. 2004, "Development and characterization of an aerosol time-of-flight mass spectrometer with increased detection efficiency", *Analytical Chemistry*, vol. 76, no. 3, pp. 712-719.
- Sullivan, R.C. & Prather, K.A. 2005, "Recent advances in our understanding of atmospheric chemistry and climate made possible by on-line aerosol analysis instrumentation", *Analytical Chemistry*, vol. 77, no. 12, pp. 3861-3885.
- Sun, J.M. & Ariya, P.A. 2006, "Atmospheric organic and bio-aerosols as cloud condensation nuclei (CCN): A review", *Atmospheric Environment*, vol. 40, no. 5, pp. 795-820.
- Takegawa, N., Miyazaki, Y., Kondo, Y., Komazaki, Y., Miyakawa, T., Jimenez, J.L., Jayne, J.T., Worsnop, D.R., Allan, J.D. & Weber, R.J. 2005, "Characterization of an Aerodyne Aerosol Mass Spectrometer (AMS): Intercomparison with other aerosol instruments", *Aerosol Science and Technology*, vol. 39, no. 8, pp. 760-770.
- Tanaka, P.L., Riemer, D.D., Chang, S.H., Yarwood, G., McDonald-Buller, E.C., Apel, E.C., Orlando, J.J., Silva, P.J., Jimenez, J.L., Canagaratna, M.R., Neece, J.D., Mullins, C.B. & Allen, D.T. 2003, "Direct evidence for chlorine-enhanced urban ozone formation in Houston, Texas", *Atmospheric Environment*, vol. 37, no. 9-10, pp. 1393-1400.
- Thomson, D.S., Schein, M.E. & Murphy, D.M. 2000, "Particle analysis by laser mass spectrometry WB-57F instrument overview", *Aerosol Science and Technology*, vol. 33, no. 1-2, pp. 153-169.
- Ulbrich, I.M., M.R. Canagaratna, Q. Zhang, D.R. Worsnop,and J.L.Jimenez. 2008, "Interpretation of Organic Components from Positive Matrix Factorization of Aerosol Mass Spectrometric Data", *Atmospheric Chemistry and Physics Discussions*, vol. 8, pp. 6729-6791.
- Volkamer, R., Jimenez, J.L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L.T., Worsnop, D.R. & Molina, M.J. 2006, "Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected", *Geophysical Research Letters*, vol. 33, no. 17.

- Yokelson, R.J., Urbanski, S.P., Atlas, E.L., Toohey, D.W., Alvarado, E.C., Crounse, J.D., Wennberg, P.O., Fisher, M.E., Wold, C.E., Campos, T.L., Adachi, K., Buseck, P.R. & Hao, W.M. 2007, "Emissions from forest fires near Mexico City", *Atmospheric Chemistry and Physics*, vol. 7, no. 21, pp. 5569-5584.
- Zelenyuk, A. & Imre, D. 2005, "Single particle laser ablation time-of-flight mass spectrometer: An introduction to SPLAT", *Aerosol Science and Technology*, vol. 39, no. 6, pp. 554-568.
- Zhang, Q., Alfarra, M.R., Worsnop, D.R., Allan, J.D., Coe, H., Canagaratna, M.R. & Jimenez, J.L. 2005, "Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry", *Environmental science & technology*, vol. 39, no. 13, pp. 4938-4952.
- Zhang, Q., Canagaratna, M.R., Jayne, J.T., Worsnop, D.R. & Jimenez, J.L. 2005, "Timeand size-resolved chemical composition of submicron particles in Pittsburgh: Implications for aerosol sources and processes", *Journal of Geophysical Research-Atmospheres*, vol. 110, no. D7.
- Zhang, Q., Worsnop, D.R., Canagaratna, M.R. & Jimenez, J.L. 2005, "Hydrocarbon-like and oxygenated organic aerosols in Pittsburgh: insights into sources and processes of organic aerosols", *Atmospheric Chemistry and Physics*, vol. 5, pp. 3289-3311.
- Zheng, J., Zhang, R., Fortner, E.C., Molina, L., Aiken, A.C., Jimenez, J.L., Gäggeler, K., Dommen, J., Dusanter, S., Stevens, P.S. & Tie, X. 2008, "Measurements of HNO3 and N2O5 using Ion drift Chemical Ionization Mass Spectrometry during the MCMA 2006 Campaign", *Atmospheric Chemistry and Physics Discussions*, vol. 8, no. 2, pp. 4877-4909.

CHAPTER V

CCN ACTIVATION STUDIES

5.1 OVERVIEW

As outlined in chapter 1, atmospheric aerosol particles influence global climate by direct and indirect processes. The direct effect of aerosols is due to the absorption, reflection, and scattering of incoming solar radiation by the particles themselves. The indirect process involves atmospheric particles serving as cloud condensation nuclei (CCN) on which water vapor condenses to form cloud droplets. The newly formed clouds then influence the incoming and outgoing radiation. The radiative forcing caused by the indirect effect of aerosol particles is highly uncertain (-0.7 [-1.8 to -0.3] W/m²) (See Figure 1-2 in Chapter 1, *IPCC*, 2007). In fact, the indirect effect of aerosol particles contributes the largest uncertainty to current estimates of the total anthropogenic forcing of the earth-atmosphere system. Therefore, particle properties that control CCN activity must be studied. In this chapter we explore the influence of shape, size, and chemical composition (i.e. solubility) on the CCN activity of aerosol particles.

Results from CCN activity experiments with three different particle types are presented: (1) highly water soluble (NH_4)₂SO₄, (2) slightly water soluble adipic acid and (3) water insoluble soot particles. The full range of water solubility expected in the ambient atmosphere can be examined through experiments with these three systems. Initial experiments were conducted on nascent, pure-component particles of each composition. To account for more complex chemical compositions encountered under ambient conditions, particles were coated with other atmospherically relevant compounds. Changes in CCN activity were monitored as a function of the amount and type of coating. The overall objective of the CCN experiments presented here is to gain a more complete understanding of the factors controlling the CCN activity of ambient

aerosol particles. As in the previous chapters, the use of multiple instrumental methods to gain a comprehensive measurement of the physical and chemical properties of the particles is a key feature of the work described.

The chapter begins with a description of Köhler theory, which relates the water supersaturation necessary for CCN activation to the physical (size) and chemical (solubility) properties of a particle. The influence of surface tension, phase, shape, and mixed composition on CCN activation theory is reviewed. The experimental apparatus used to generate, coat, and analyze the particles is then described with an emphasis on the utility of combining measurements from multiple instruments to fully characterize the particle properties of interest. Results from CCN experiments with the three particle systems; (NH₄)₂SO₄, adipic acid, and soot are then presented. Results are discussed in the context of how the laboratory measurements can be used to inform ambient aerosol CCN activation.

Part of this chapter is published in Hings, S.S., Wrobel, W.C., Cross, E.S., Worsnop, D.R., Davidovits, P. & Onasch, T.B. 2008, "CCN activation experiments with adipic acid: effect of particle phase and adipic acid coatings on soluble and insoluble particles", Atmospheric Chemistry and Physics, vol. 8, no. 14, pp. 3735-3748.

5.2 BACKGROUND AND THEORY

Particles emitted at the surface of the earth are transported upwards in the atmosphere via convective mixing. As a result, the particles pass through regions of air where the water vapor content is higher than 100% relative humidity (*i.e.* supersaturated). Due to this supersaturated air, water vapor may condense onto the particles causing them

to grow into cloud droplets ($d_p \sim 10 \ \mu m$). Whether a given particle will form a cloud droplet depends upon the water vapor pressure over the surface of the particle and the chemical composition and size of the particle itself. Standard Köhler theory describes the condensational growth of a particle of known composition and size as a function of the supersaturation ratio S_w (*Pruppacher and Klett*, 1997):

$$S_{w} = \frac{p}{p_{0}} = \gamma_{w} x_{w} \exp(\frac{4M_{w}\sigma}{RT\rho_{w}d_{p}})$$
(5-1)

Here, p is the vapor pressure of water over the solution droplet, p_0 is the equilibrium vapor pressure over a flat surface, γ_w is the activity of water, x_w is the mole fraction of water in the aqueous solution, M_w is the molar mass of water, σ is the surface tension of the solution droplet, R is the universal gas constant, T is the temperature, ρ_w is the density of water, and d_p is the diameter of the droplet at water vapor pressure p. This diameter will be designated as the solution droplet diameter.

The product $\gamma_w x_w$ represents the Raoult (or solution) effect, which increases with increasing wet diameter d_p . The exponential term represents the Kelvin (or curvature) effect, which decreases with increasing wet diameter. These two competing effects result in a maximum with respect to d_p for Eq. (5-1) (See Figure 5-1).

The term commonly used to describe particle growth by vapor condensation is supersaturation (*S*, in percent) defined as:

$$S = (S_w - 1) \cdot 100 \tag{5-2}$$

Figure 5-1 displays *S* as a function of the solution droplet diameter d_p for a particle composed of adipic acid with an original dry diameter of 145 nm. The maximum of this curve is known as the critical supersaturation (*S_c*). For a 145 nm adipic acid

particle $S_c = 0.166\%$, implying that this particle would act as a CCN if the ambient supersaturation were greater than 0.166%. Standard Köhler theory describes the activation of single-component aqueous solution droplets and is used here to model the CCN activity of (NH₄)₂SO₄ and completely dissolved adipic acid.



Figure 5-1. Calculated supersaturation *S* as a function of the solution droplet diameter d_p for a particle composed of adipic acid. The adipic acid particle has dry diameter 145 nm and a critical supersaturation S_c of 0.166%.

5.2.1 Influence of Surface Tension on S_c

Surface tension is a key parameter for calculating the supersaturation (S_w) and therefore the critical supersaturation (S_c) (See Eq. 5-1 and 5-2). It has been shown that dissolved, surface active, slightly soluble organic compounds can lower the surface tension of aqueous solutions, depending on concentration, by as much as one third (*Shulman et al.*, 1996 and *Facchini et al.*, 2000). A decrease in σ lowers the critical supersaturation as predicted by Köhler theory.

The surface tension of an adipic acid solution can be calculated from the Szyszkowski-Langmuir equation as has been done by Henning et al. (2005):

$$\sigma = \sigma_w(T) - aT\ln(1 + bC) \tag{5-3}$$

Here, *C* is the concentration of dissolved carbon (moles of carbon per kg of water) and $\sigma_w(T)$ is the surface tension of water at temperature *T*. The parameters *a* and *b* are obtained by fitting the experimental results to Eq. 5-3. For pure adipic acid, Henning et al. (2005) obtained *a* = 0.0106 and *b* = 11.836.

5.2.2 Mapping S_c as a Function of Particle Size and Composition

To display the full range of CCN activity observed for particles in the ambient atmosphere it is necessary to determine S_c for the range of particle sizes and water solubilities expected in the atmosphere. Using Eqs 5-1 and 5-2, S_c values were calculated as a function of dry particle diameter for ammonium sulfate, adipic acid, and an insoluble but wettable substance. Results are shown in Figure 5-2. Ammonium sulfate is modeled using the surface tension of water (0.072 J/m²) and represents a lower limit to CCN activity observed in the atmosphere. In other words, ammonium sulfate particles will activate to form water droplets at lower supersaturations, as compared to other atmospheric species. Adipic acid is modeled with both the concentration-dependent surface tension defined by the Szyszkowski-Langmuir equation (Eq. 5-3; ranging from 0.060- 0.072 J/m² for 30-300 nm adipic acid particles) and the surface tension of water (0.072 J/m²). The black line in Figure 5-2 is the critical supersaturation for a pure water droplet. This line models the growth of an insoluble but wettable spherical surface and is hereafter referred to as the "wettable line". The wettable line represents an upper limit of CCN activity observed in the atmosphere. The range of S_c values and dry particle diameters plotted in Figure 5-2 encompass the range of conditions expected in the atmosphere. Therefore, Figure 5-2 serves as the map for displaying and interpreting the experimental data discussed in the following sections.



Figure 5-2. Critical supersaturations as a function of initially dry particle diameter, calculated from Köhler theory for ammonium sulfate (red), adipic acid (yellow) and an insoluble but wettable substance (black). The lines for adipic acid have been modeled in two different ways: using the surface tension of water (dashed line) and using a concentration-dependent surface tension defined by the Szyszkowski-Langmuir equation (solid line). See text for details.

5.2.3 Role of Particle Phase in Activation of Single-Component Aerosols

Bilde and Svenningsson (2004) studied the role of phase in the CCN activation of adipic acid particles and found that deliquesced ("wet") adipic acid droplets activate at lower S_c than initially dry adipic acid particles. Kreidenweis et al. (2006) suggested that below a certain particle diameter, deliquescence of initially dry organic compounds of low water-solubility occurs at higher water vapor pressure than the critical supersaturation for CCN activation. In such a case, there is an activation barrier to the onset of cloud droplet growth governed by the deliquescence of the organic species (*Hori* *et al.*, 2003, and *Broekhuizen et al.*, 2004). Therefore, two CCN activation regimes are identified for particles composed of slightly soluble organic compounds. For larger particles, CCN activation is governed by the Köhler theory. For relatively smaller particles, the CCN activation is governed by the deliquescence transition. The deliquescence pressure ratio, given by (*Pruppacher and Klett*, 1997), is

$$\frac{p}{p_0} = \gamma_w \exp\left(\frac{4\sigma_{sat}M_w}{d_d\rho_w RT}\right)$$
(5-4)

Here, σ_{sat} is the surface tension of the saturated droplet, and d_d the dry particle diameter. We note that the surface tension used in Eq. 5-4 is that of a saturated solution whereas in Eq. 5-1, the solution need not be saturated.

The % deliquescence supersaturation S_{del} is obtained in a way analogous to Eq. 5-2. For smaller particles and certain single-component, low water-soluble organic aerosols (including adipic acid) the parameter S_{del} can be larger than the predicted critical supersaturation calculated via Eqs. 5-1 and 5-2. When $S_{del} > S_{c, calculated}$, cloud-droplet activation is controlled by the deliquescence of the particles and activation occurs when the water vapor pressure is high enough to cause particle deliquescence, that is, CCN activation occurs at S_{del} . However, when the condition is reached such that $S_{del} < S_{c, calculated}$, cloud-droplet activation occurs at $S_{c, calculated}$. In short, a single-component adipic acid aerosol will only activate as a CCN after the particle has deliquesced. The water vapor pressure at which a particle will deliquesce (at the calculated S_{del} value) is also known as its deliquescence relative humidity (DRH). It must be noted that CCN activation can only occur at the S_{del} when the particle is initially dry and when $S_{del} > S_{c, calculated} = S_{c, calculated}$. *calculated.* Initially wet particles have already deliquesced and therefore will activate at the S_c value predicted by Köhler theory.

Figure 5-3 shows deliquescent supersaturations S_{del} as a function of dry particle diameter calculated from Eq. 5-4 using water activities of $\gamma_w = 0.990$ and $\gamma_w = 0.997$. The deliquescent curves are strongly dependent on γ_w . For example, at $S_{del} = 0.3\%$, a particle with a water activity of 0.990 will deliquesce at 165 nm whereas a particle with a water activity of 0.997 will deliquesce at diameter 298 nm.

Reliable activity data for adipic acid are not available and therefore activity must be calculated based on solubility and molecular weight. Using a bulk solubility of 25 g/L, Kreidenweis et al. (2006) calculated the activity coefficient of adipic acid to be 0.997. The quoted solubility is accurate to only two figures. Therefore, the activity coefficient is not likely to be more accurate. In Figure 5-3 we show calculated deliquescence curves for activity coefficients of 0.990 (gray) and 0.997 (green). The indicated borders for each γ_w are calculations with the two limits of surface tension quoted in the text (σ between 0.060 and 0.072 J/m²). As will be shown in Section 5.4.2, $\gamma_w = 0.990$ provides a better fit to our experimental results.



Figure 5-3. Calculated deliquescent supersaturations S_{del} (plotted on the S_c axis) as a function of the dry particle diameter for adipic acid using water activities of 0.990 (gray) and 0.997 (green). The upper bound for each activity corresponds to a surface tension of 0.072 J/m² while the lower bound corresponds to a surface tension of 0.060 J/m².

5.2.4 Determination of the Particle Shape Factor

Particle shape can influence the CCN activity of atmospheric aerosols. Because the methods of aerosol generation used in this and other studies may produce particles that are not spherical, the shape factor needs to be considered in CCN activity measurements. Observation of the shape of aerosol particles is usually performed with electron microscopy. Such observations are complicated because it is difficult to collect the particles without altering their shape. Several attempts were made to observe the particles used in this study with a scanning electron microscope. However, no consistent or reliable data were obtained. Therefore, tandem SMPS-AMS measurements were used to measure the dynamic shape factor. As described in detail in Chapter 2, Section 2.2.2, this method involves selecting particles by mobility with a DMA and measuring the resulting mobility diameter (d_m) and vacuum aerodynamic diameter (d_{va}) distributions with an SMPS and AMS respectively. The combined measurements of d_{va} and d_m can be used to determine the particle dynamic shape factor (χ).

The general expression for relating d_{va} and d_m measurements is:

$$\frac{\frac{d_{va} \cdot \chi_{v} \cdot \chi_{t} \cdot \rho_{0}}{\rho_{p}}}{C_{c} \left(\frac{d_{va} \cdot \chi_{v} \cdot \rho_{0}}{\rho_{p}}\right)} = \frac{d_{m}}{C_{c} (d_{m})}$$
(5-4)

Here, χ_{ν} and χ_t are the dynamic shape factors in the free molecular and the transition regimes, ρ_0 is unit density, ρ_p is the particle density, and $C_c(d)$ is the Cunningham slip correction factor. If one assumes that $\chi_t = \chi_{\nu}$ then for a known particle density ρ_p (which is equal to ρ_m for particles without internal voids), the dynamic shape factor χ of the particles can be estimated (*DeCarlo et al.*, 2004). The dynamic shape factor χ is equal to unity for spherical particles without internal voids and larger than unity for nonspherical particles. Results of these shape factor determinations are discussed in Section 5.4.2.3

5.2.5 Considerations for CCN Activity of Coated Ammonium Sulfate Particles

In the present work, the activation of ammonium sulfate particles coated by initially dry adipic acid is also studied. In such a case, the possibility exists that the droplet contains an undissolved adipic acid core surrounded by a solution of water, adipic acid, and ammonium sulfate. The presence of the ammonium sulfate allows condensational growth of the particle by addition of water without causing the complete deliquescence of the adipic acid. The presence of such a slightly soluble core that gradually dissolves as the droplet grows modifies the overall shape of the Köhler growth curve. Shulman et al. (1996) modified the standard Köhler theory to describe the effect of such a mixed composition on the activation of an aerosol particle into a cloud droplet. Our modeling calculations show that under our experimental conditions, the predictions of the standard and modified Köhler theories are the same.

5.3 EXPERIMENTAL

5.3.1 Apparatus

A schematic diagram of the experimental apparatus is shown in Figure 5-4. The main components of the set-up are: A particle generation system, a particle coating system, two differential mobility analyzers (DMA I, TSI Model 3071A, and DMA II, TSI Model 3080), a condensation particle counter (CPC, TSI Model 3010), a continuous-flow streamwise thermal-gradient CCN counter (CCNC, Droplet Measurement Technologies), and a Time-of-Flight Aerosol Mass Spectrometer equipped with a light scattering module (LS-ToF-AMS).



Figure 5-4: Schematic of experimental apparatus used during the CCN experiments.

The operating details of the DMA, CPC, LS-ToF-AMS, and CCNC were described in Chapter 2. Here an overview of the CCNC instrument is provided along with an explanation of how S_c is determined.

5.3.2 Cloud Condensation Nuclei Counter

The DMT (Droplet Measurement Technologies) Cloud Condensation Nuclei Counter (CCNC) used in this study is operated in a continuous flow mode. That is, the instrument provides fast sampling by continually monitoring the CCN activity of the particles passing through it. The instrument is capable of generating nearly constant values of supersaturation between 0.07% and 3.7%. The stated accuracy of these supersaturation values is $\pm 2\%$ Supersaturation is easily controlled and maintained, making it possible to scan the full range of supersaturations for a given particle size.

The aerosol flow introduced into the CCNC instrument is split into an aerosol and a sheath flow. The sheath flow is filtered, humidified and heated. This sheath flow

constrains the main aerosol flow to the centerline of the cylindrical CCNC column. The inner wall of the CCNC column is continually wetted and a positive temperature gradient dT is applied to the CCNC column in the direction of the flow. Water vapor supersaturation is therefore generated along the centerline of the CCNC column (due to the difference in diffusion rates between water and heat). Particles begin to grow at the point when the supersaturation inside the instrument is equal to S_c . Droplets that grow to diameters larger than 1 µm are detected by an optical particle counter (OPC) at the exit of the column and are defined as CCN active particles.

The supersaturation in the CCNC column is primarily a function of the temperature difference (dT) between the top (upstream) and the bottom (downstream) of the CCNC column. It also depends on the flow and the pressure inside the instrument. The relationship between supersaturation (S) and the measured temperature difference (dT) inside the CCN column is determined by calibration with ammonium sulfate particles at a specific flow and pressure. To obtain reliable experimental results, the CCNC apparatus was carefully calibrated before and after each CCN experiment. Specific details relevant to the calibration measurements used for the current work are presented in Appendix 5A.

5.3.3 Measurement of S_c

After particle generation and size-selection, the aerosol flow is iso-kinetically split between the DMA II/CCNC system (2.0 Lpm) and LS-ToF-AMS system (0.08 Lpm). Before and after each CCN experiment (i.e., every time a new particle size is selected), DMA II and the CPC are used as a scanning mobility particle sizer (SMPS) to
measure the size distribution of the particles (See section 2.2.2 for a description of the SMPS). When measuring the CCN activity of a certain particle type, the particles are size-selected a second time with DMA II in accord with the mode diameter determined during the SMPS scan. In this way the function of the second DMA switches between scanning and size selecting the distribution. When the particles are uncoated, the mode diameter of the SMPS trace is the same as the diameter selected with DMA I. However, when the particles are coated, DMA II selects the coated diameter of the particles. The resulting monodisperse aerosol flow exiting DMA II is split between the CCNC (1.0 Lpm) and the CPC (1.0 Lpm).

The supersaturation in the CCNC is varied between 0.07% and 3.7% by setting the CCNC instrument *dT* between 1.5 and 27 K. During all experiments, the CCNC was operated at a total flow rate of 1 Lpm.

The fraction of CCN activated aerosol is the ratio of the number concentration of CCN droplets measured by the CCNC (N_{CCN} , number of particles that grow larger than 1 μ m, detected by the optical particle counter (OPC)), to the total number concentration of particles measured by the CPC (N_{CPC}). The critical supersaturation at a particular aerosol size is defined as the supersaturation at which 50% of the particles grow into droplets

(when
$$=$$
 $\frac{N_{CCN}}{N_{CPC}} = 0.5$).

The method of determining the critical supersaturation (S_c) is illustrated in Figure 5-5 that shows examples of activation curves measured for 45 nm and 31 nm ammonium sulfate. The curves are generated by measuring the fraction of activated aerosol and plotting this number as a function of the temperature difference dT in the CCNC column.

The plot is fitted with a sigmoid function to find the critical temperature difference (dT_c) where the activated fraction is 0.5. The critical supersaturation is then calculated from the calibration curve described in Appendix 5A. The width of the sigmoidal curve is due to the spread in the aerosol size distribution determined by the flow conditions and subsequent transmission function of DMA I.



Figure 5-5: Sample activation curves for 31 nm (red) and 45 nm (blue) ammonium sulfate particles. The critical supersaturation (S_c) calculated from the critical temperature (dT_c) is the supersaturation where 50% of the particles are activated.

5.3.4 Combining Measurements of CCN activity with SMPS and AMS Measurements

The CCNC measurement of the S_c is a function of the particle composition, size, shape, density and phase (liquid or solid). In these experiments, the CCN measurement is combined with measurements of the non-refractory chemical composition, vacuum

aerodynamic diameter and mobility diameter. In this way, measured changes in CCN activity are directly correlated with changes in particle shape, density, and chemical composition.

5.3.5 Summary of Particle Generation Techniques

One critical aspect of the experimental apparatus is the stable and reproducible generation of each particle type of interest. In this section the particle generation methods for ammonium sulfate, adipic acid, and soot particles are reviewed. Each particle system studied starts with the generation of a polydisperse size distribution of particles. This distribution is size selected with DMA I, and the resulting monodisperse distribution of particles is then characterized with the CCNC-SMPS-AMS instruments. In the case of coated particles, the monodisperse distribution of particles from DMA I, is passed over a heated reservoir containing the coating material. The temperature of the reservoir is adjusted to vary the thickness of the coating.

5.3.5.1 Ammonium Sulfate Particles

Ammonium sulfate particles are generated by atomizing aqueous solutions of ammonium sulfate and passing the solution droplets through diffusion driers as shown in Figure 5-4.

5.3.5.2 Adipic Acid Particles

Adipic acid particles are generated by three different methods: (1) atomization of aqueous solutions of adipic acid, (2) homogeneous nucleation of adipic acid vapor, and (3) condensation of adipic acid vapor onto ammonium sulfate seeds.

In the case of homogeneous nucleation, adipic acid is heated in a round-bottom flask to approximately 150 °C. The airflow through the nucleation region is 2 L/min. The particles nucleate as the vapor is passed through a water-cooled condenser. This generation method provides a stable concentration of pure dry (solid) adipic acid particles which are then size selected with DMA I.

For the adipic acid particles generated via condensation onto ammonium sulfate seeds, the ammonium sulfate cores are first generated by atomization of an aqueous solution. Prior to coating with adipic acid, the sulfate particles are dried and size selected with DMA I (d_m core = 30 nm). The sulfate particles are coated via vapor deposition as they pass through a heated reservoir containing adipic acid. The coating thickness of adipic acid is controlled by the temperature of the reservoir.

Upon entering the CCNC column, the highly water-soluble ammonium sulfate core absorbs enough water to completely dissolve the adipic acid, forming a concentrated adipic acid-ammonium sulfate aqueous solution. We postulate that water reaches the ammonium sulfate core either via diffusion through the adipic acid coating or by passage through imperfections in the coating. Experiments as well as calculations (Section 5.4.2) show that if the mass fraction of the ammonium sulfate core is small (< 15%), this method provides an aerosol particle that, from the perspective of CCN activation, can be considered to be a single-component 'wet' adipic acid particle.

5.3.5.3 Soot Particles

Soot particles are produced in a commercial McKenna burner by combustion of ethlyene and oxygen, pre-mixed with a dilution flow of nitrogen (*Slowik*, 2006; *Slowik*, *Cross et al.*, 2007a; *Slowik*, *Cross et al.*, 2007b; *Cross et al.*, 2008; *Wrobel*, 2008).

Depending on the operating conditions of the flame (*i.e.* the ratio of fuel to oxygen), soot particles of different chemical composition and morphology are produced. For the CCN experiments described here, soot cores were produced at low (2.0) and high (5.0) fuel-to-air equivalence. The low equivalence ratio condition produced fractal soot particles, primarily composed of black carbon (~ 95% by mass). The high equivalence ratio condition produced spherical soot particles composed of ~ 50% black carbon and ~ 50% non-refractory organic material (aliphatics and polycyclic aromatic hydrocarbons (PAHs) condensed onto the surface of the black carbon core). For each type of soot particle, polydisperse distributions were size selected with DMA I. The size-selected soot particles were then coated by passing the particles over a heated reservoir containing the coating material of interest.

5.4 RESULTS AND DISCUSSION

5.4.1 Experiments with Ammonium Sulfate

Ammonium sulfate is prevalent in the atmosphere as a by-product of coal and fuel combustion processes. It is one of the most water soluble species found among atmospheric particles. Köhler theory indicates that pure ammonium sulfate particles with dry diameters greater than 50 nm readily activate at supersaturations $\geq 0.5\%$ (See Figure 5-2). Supersaturations of this magnitude are routinely encountered in the ambient atmosphere, suggesting that cloud formation will readily occur if ammonium sulfate particles are present.

Ammonium sulfate particles rarely exist in the ambient atmosphere as pure ammonium sulfate. Instead, sulfate is routinely mixed with other chemical components (primarily organic) which influence the water solubility and subsequent CCN activity of the particles.

To gain insight into the CCN activation of ambient particles with a range of residence times in the atmosphere, ammonium sulfate particles of known size were coated with atmospherically relevant organic compounds. The organics were chosen on the basis of water solubility and phase and included adipic acid, oleic acid, dioctyl sebacate (DOS), and stearic acid. In each experiment, the SMPS-AMS-CCNC instrument combination provided measurements of the shape, size, non-refractory composition and S_c of the coated particles.

As stated previously adipic acid is a slightly soluble organic solid. The first series of coating experiments used adipic acid to determine the influence of a slightly soluble compound on the CCN activity of ammonium sulfate. The second series of CCN experiments tested the influence of two insoluble organic liquids: oleic acid and dioctyl sebacate (DOS). The third set of experiments coated the sulfate particles coated with stearic acid, an insoluble organic solid. The combined results provide a comparison between the influence of insoluble solid and liquid organic coatings on the CCN activation of ammonium sulfate particles. Where possible, experimental data points are compared with model critical supersaturation curves obtained with modified Köhler theory.

5.4.1.1 Adipic acid-coated ammonium sulfate particles

Adipic acid is a slightly soluble organic compound with a water solubility of ~ 25 g/L. For reference, ammonium sulfate has a water solubility of 70.6 g/100 mL. Three ammonium sulfate cores $d_{core} = 34$, 53 and 73 nm were coated with adipic acid (coating thickness ~5-34 nm). The CCN activity of the coated particles was measured as a function of the total particle size (ammonium sulfate core + adipic acid coating). The results show that as more and more adipic acid is added to the sulfate particles, the coated particles tend to show CCN activation typical of pure adipic acid particles (See Figure 5-6). The transition from the ammonium sulfate activation line to the adipic acid activation line follows the paths modeled with modified Köhler theory (shown as the dashed lines in Figure 5-6). This indicates that the CCN activity of the coated ammonium sulfate particle is reasonably modeled by the calculation using modified Köhler theory that accounts for the combined water activity of the solution droplet.

In all three cases, the uncoated ammonium sulfate particle activates on the ammonium sulfate Köhler theory line, even though the particle is initially a dry solid. Under these conditions, the calculated S_c is greater than the water vapor pressure at which particle deliquescence occurs. Ammonium sulfate particles deliquesce readily and the water vapor pressure in the CCNC instrument is always above the deliquescence vapor pressure for ammonium sulfate. As expected, with increasing adipic acid coating thickness, the measured S_c values rise above the ammonium sulfate Köhler theory line and approach the adipic acid Köhler theory line.



Dry Particle Diameter (nm)

Figure 5-6: S_c plotted as a function of particle diameter for adipic acid coated ammonium sulfate particles of sizes $d_{core} = 34$ nm (black), 53 nm (green) and 73 nm (blue) The dashed lines are calculated using Köhler theory.

5.4.1.2 Oleic acid-coated and DOS-coated ammonium sulfate

Both oleic acid and DOS have very low water solubilities. Each organic material is a liquid and will likely form a uniform coating around the ammonium sulfate core. In this set of experiments, a 71 nm ammonium sulfate core was coated with oleic acid and a 46 nm and a 76 nm ammonium sulfate core was coated with DOS. For each organic coating, modified Köhler theory was used to model the CCN response of the ammonium sulfate core to the different coating thicknesses. In each case the liquid organic coating was considered to have a water solubility of 0.1 kg/mL. The experimental and model data are displayed in Figure 5-7.



Figure 5.7: S_c plotted as a function of particle diameter for oleic acid (pink diamonds) and DOS (green circles) coated ammonium sulfate particles. The dashed lines are calculated using modified Köhler theory using a water solubility of 0.1 kg/mL for each of the coating materials.

The data displayed in Figure 5-7 show excellent agreement between the measured and modeled results for both the DOS and oleic acid coatings. This agreement implies that, on the timescale of our experimental procedures, water is able to gain access to the ammonium sulfate core and cause activation to a cloud droplet. Further, even though the DOS and oleic acid coatings essentially insoluble, $a \sim 30$ nm liquid organic coating thickness is not sufficient to block CCN activation.

5.4.1.3 Stearic-acid coated ammonium sulfate

Stearic acid was used to test the influence of a solid insoluble coating on the CCN activation of the ammonium sulfate particles. Experimental data for three ammonium sulfate cores ($d_{core} = 37, 55, \text{ and } 76 \text{ nm}$) coated with 50-100 nm of stearic acid are shown in Figure 5-8.



Dry Particle Diameter (nm)

Figure 5-8: S_c plotted as a function of particle diameter for stearic acid-coated ammonium sulfate particles of sizes $d_{core} = 37$ nm, 55 nm and 76 nm.

In contrast to the adipic acid, oleic acid and DOS experiments, the stearic acid coatings result in an increase in S_c (the amount of water vapor necessary to cause CCN activation) with increasing coating thickness. It appears that the CCN activity of the ammonium sulfate core is shut down due to the stearic acid coating. One explanation for this observation is that the ammonium sulfate core has become encapsulated within a shell of stearic acid. As a result, on the time scale of the experiment (residence time of the coated particles in the CCNC column) water vapor cannot access the hygroscopic core, and the CCN activation is consequently inhibited. Further experiments with insoluble solids such as stearic acid, must be completed to quantify the influence of water insoluble coatings on the CCN activity of ammonium sulfate aerosol particles.

5.4.1.4 Conclusions for CCN activation experiments with coated ammonium sulfate.

The experiments with adipic acid-coated ammonium sulfate aerosol particles indicate that the addition of a small mass fraction of a hydrophilic soluble compound (e.g. ammonium sulfate) to dry adipic acid particles eliminates the effect of particle phase on CCN activation, in agreement with Bilde and Svenningsson (2004). The data suggest that if ammonium sulfate particles are coated with slightly soluble organic solids in the atmosphere, their CCN activation will be controlled by the volume additive solubility of the mixed particle. Cloud condensation nuclei experiments with ammonium sulfate particles coated with insoluble liquid organic material indicate that water vapor is capable of accessing the hygroscopic core and forming cloud droplets with coating thickness of ~ 50 nm liquid organic. In all cases, the CCN activation is effectively modeled with a liquid organic water solubility of 0.1 kg/mL. Insoluble solid organic coatings begin to

shut down CCN activity of ammonium sulfate particles after ~ 25 nm coating thickness. The results from the ammonium sulfate coating experiments demonstrate that relatively small changes in the chemical composition can significantly alter the CCN activity of a given particle. The observations presented in this section underlie the importance of understanding how aerosol particles change as they are processed in the atmosphere.

5.4.2 Experiments with Adipic Acid

The purpose of the work with adipic acid is to understand the factors governing the CCN activity of slightly soluble organic compounds and to explain the wide variations in the published critical supersaturation measurements for adipic acid. The current work spans the conditions of the previous studies and also provides alternate methods for producing 'wet' and dry adipic acid particles without the need to produce them by atomization of aqueous solutions.

The previous 11 published studies of adipic acid generated the adipic acid particles by atomization of aqueous solutions. In order to explore the full range of experimental conditions, adipic acid particles were generated by atomization and by condensation of adipic acid vapor. The following measurements were performed to study the CCN activity of adipic acid:

(1) CCN activity of dry adipic acid particles generated by atomization.

(2) CCN activity of dry adipic acid generated by homogeneous nucleation (condensation of adipic acid vapor).

(3) CCN activity of wet adipic acid particles generated by atomization.

(4) CCN activity of wet adipic acid particles generated by vapor deposition of a mass fraction of >85% adipic acid on small ammonium sulfate cores. (This method of generating wet adipic acid is discussed in detail.)

5.4.2.1 Previously published S_c data for adipic acid

Figure 5-9 shows published adipic acid critical supersaturation data as a function of particle diameter from 11 studies. In all experiments, particles were formed by atomizing aqueous solutions of adipic acid. Particles were subsequently dried to relative humidities between 5 and 20%. In one case only, particles were kept wet as supersaturated (i.e., deliquesced) solution droplets (designated in the figure as "wet"). In one set of experiments, Rissman et al. (2007) heated the adipic acid particles prior to drying them.



Figure 5-9. Published critical supersaturations (S_c) for adipic acid as a function of dry particle size. Particles were obtained by atomizing aqueous solutions. The source of the

data is shown by the symbols as identified in the insert. The state of the particles prior to activation was dry unless otherwise noted. Critical supersaturations predicted by the standard Köhler theory are shown as solid lines for ammonium sulfate (red line), adipic acid (orange line), and an insoluble but wettable substance (black line). See text for details.

The published data for adipic acid exhibit significant scatter. For example, at 1% supersaturation, measured critical diameters for adipic acid particles vary from 50 nm to 180 nm. The measurements of Bilde and Svenningsson (2004) for wet particles fall close to the standard Köhler theory line for adipic acid. The measurements of Rissman et al. (2007) for the largest sized particles approach the predictions of the Köhler theory. All other data show higher critical supersaturations than predicted by the Köhler theory. The large variations in measured supersaturation are likely caused by particle phase differences (*Bilde and Svenningsson*, 2004), differences in particle preparation (*Rissman et al.*, 2007), as will be discussed, and also possibly due to methods of CCN measurement (see Appendix 5A).

5.4.2.2 Dry Adipic Acid Particles Generated by Atomization

In this set of experiments, the CCN activation of adipic acid particles (50 nm $< d_m$ < 250 nm) generated by atomization of adipic acid solutions is measured. About 15 such independent experimental CCN activation experiments were conducted. Reproducible data sets with adipic acid aerosols produced by atomization were not obtained and the cause of this irreproducibility was not determined. Most likely the scatter in the data is due to trace impurities in the solution which we were not able to completely eliminate.

5.4.2.3 Homogenously Nucleated Dry Adipic Acid Particles

The results of CCN activation experiments with dry adipic acid particles generated by homogeneous nucleation of adipic acid vapor are shown in Figure 5-10 as blue points. Here, the measured critical supersaturation (S_c) is shown as a function of dry particle diameter (d_d). Each critical supersaturation value in the figure is the average of at least three measurements for every dry particle diameter (the standard deviation is indicated by the error bars). Measurements were conducted over a period of several days to ensure reproducibility. The standard deviation of the measurements is in all cases except one less than 4% of the measured S_c values.

The solid lines are the same calculated Köhler lines shown in Figures 5-1 and 5-3. The shaded area models the deliquescence of the particles according to the Kelvin equation (Eq. 5-4) as discussed in section 5.2. The surface tension of saturated aqueous adipic acid droplets larger than 40 nm is calculated to have values between 0.060 and 0.072 J/m² (See Eq. 5-3). A water activity over a saturated adipic acid solution of $\gamma_w = 0.99$ was chosen to provide a best fit to the experimental data. The borders of the shaded

region are obtained with the two limiting values of calculated surface tension (0.060 and 0.072 J/m^2).



Figure 5-10. *S_c* plotted as a function of particle diameter for dry adipic acid particles (blue symbols). Köhler theory lines are the same as in Figures 5-1 and 5-3. The shaded area is the deliquescence region calculated from Eq. 5-4 with $\gamma_w = 0.990$. The upper and lower bounds correspond to solution surface tensions of 0.072 and 0.060 J/m², respectively.

As is evident, the CCN activities of particles smaller than 150 nm in diameter are not governed by standard Köhler theory. The activation of the smaller particles more closely follows the predictions of the deliquescence calculations, although the fit is not exact. Still, the general trend in the measurements for adipic acid particles smaller than 150 nm follows the deliquescence model, supporting the suggestion of Hori et al. (2003) and Kreidenweis et al. (2006) that deliquescence-controlled activation may govern droplet formation for small, slightly soluble organic particles. The smallest particle ($d_m = 88 \text{ nm}$) in this set of measurements behaves as a particle composed of an insoluble wettable material. We could not obtain data for particles smaller than $d_m \sim 88 \text{ nm}$ because to produce such small particles with our homogenous nucleation apparatus, we had to reduce the adipic acid vapor pressure to a point where the number of particles produced was too small to perform CCN experiments. The activation of particles larger than ~150 nm follows standard Köhler theory.

As described in section 5.2.4, the dynamic shape factor χ of the particles can be estimated from SMPS, AMS size measurements via Eq. 5-4. Using the adipic acid bulk density of 1.36 g/cm³, we estimate the dynamic shape factors to be as shown in Table 5-1. The use of bulk density in Eq. 5-5 assumes that the particle does not contain internal voids. This seems to be a reasonable assumption for particles that are formed by vapor condensation. The uncertainties in χ are primarily due to the uncertainty in the measured vacuum aerodynamic diameter (d_{va}), which is approximately \pm 15%. Within these error limits, the particles do not appear to deviate significantly from a spherical shape ($\chi = 1.0$).

d_m	$\chi \pm \Delta \chi$
100	1.04 ± 0.16
125	1.10 ± 0.19
151	1.22 ± 0.19
188	1.24 ± 0.19
200	1.26 ± 0.19

Table 5-1: Estimated particle dynamic shape factors as a function of particle size for dry adipic acid generated by homogeneous nucleation.

5.4.2.4 Comparison with Previous Studies

The CCN activation curve for the nucleation-generated dry adipic acid is combined with the previously published CCN activation data for dry adipic acid in Figure 5-11.



Figure 5-11: S_c plotted as a function of particle diameter for dry adipic acid particles from previously published studies (as in Figure 5-1) shown together with our measurements.

Some of the published S_c measurements are above and some are below the value for the nucleated adipic acid. The wide scatter in the measured CCN activity obtained in the previous studies suggests that some significant parameter or parameters vary from experiment to experiment. Our experiments do not provide an explanation for these discrepancies, however we can suggest some possible factors that may affect the results. Because all previously published experiments were performed with aerosol generated by atomization, it is possible that solution impurities are one cause of the scatter in the data. Note that all the previously obtained S_c results fall above the Köhler curve. That is, the data points are all within the region where deliquescence governs the onset of activation. Therefore, if impurities are the cause of the scatter, they must be such that some promote and others hinder particle deliquescence.

Another possible reason for the scatter in the published measurements of S_c may be related to the shape of the particles produced by the atomization and drying process. The volume-equivalent diameter (d_{ve}) of a non-spherical particle is smaller than its electrical mobility diameter (d_m) (*DeCarlo et al.*, 2004). In all the published measurements, the reported diameter is the mobility diameter as measured by a DMA instrument. If the atomization-generated particles are non-spherical, their effective diameter is smaller than their measured d_m . Were this the case, the data points would be shifted to the left (i.e., to a smaller effective diameter) placing the published data closer to the results obtained in our studies. A possible confirmation of this hypothesis is provided by the data of Rissman et al., (2007) which plots data for both heated and unheated adipic acid particles. The heated adipic acid particle shave a smaller effective diameter than the unheated particles). This might be due to a reorganization of the adipic acid during heating, resulting in more spherical adipic acid particles.

As is shown in Appendix 5A, the calibration of the CCNC instrument is a critical part of these experiments. Slight miscalibrations of the CCNC instrument prevent accurate measurements of S_c values. Variations in the calibration of the CCN instrument

from one experimental group to another cannot be ruled out as one of the causes for the scatter in the data.

5.4.2.5 Wet Adipic Acid

As is shown in Figure 5-11, there is only one previously published CCN activation study for wet adipic acid aerosol particles. The results of the published study are in agreement with standard Köhler theory. As stated earlier, consistent measurements with either wet or dry adipic acid aerosol produced by atomization were not obtained. Most of our wet adipic acid measurements (from 5 independent runs) fell below the critical supersaturation predicted by the Köhler theory. We attribute the scatter in these data to residual impurities, most likely ammonia, which can play a role in experiments with wet adipic acid produced by atomization. The CCN activity of initially dry adipic acid, however, is reported to be unaffected by ammonia (*Dinar et al.*, 2008).

To eliminate possible impurities in the adipic acid particles (such as contamination by ammonia resulting from the atomization process), we generated effectively wet adipic acid aerosol by coating small ammonium sulfate cores with adipic acid by vapor deposition (described as particle type (4) in section 5.4.2). Experiments were conducted with three ammonium sulfate core sizes ($d_{core} = 34$ nm, 53 nm, 73 nm) coated with adipic acid. In this subset of experiments, the adipic acid mass fraction was in all cases greater than 0.85. Under these conditions, the calculated S_c of the dual-component aerosol particle is the same to within 10% as the S_c of a single-component adipic acid particle of equivalent diameter. A plot of S_c as a function of wet adipic acid

particle diameter is shown in Figure 5-12. Data from the present work are displayed as blue points. Data of Bilde and Svenningsson (2004) are shown as light blue stars. As is evident, the data are in accord with standard Köhler theory.



Figure 5-12: Plot of S_c as a function of wet adipic acid particle diameter. Data from present work are displayed as blue points. Data of Bilde and Svenningsson (2004) are shown as light blue stars.

5.4.2.6 Conclusions of CCN activity experiments with adipic acid

The CCN activity of both dry and 'wet' (deliquesced solution droplets) adipic acid particles and the effect of adipic acid coatings on the CCN activity of soluble and insoluble particles were determined. The results of the experiments lead to the following conclusions: In accord with earlier suggestions (*Hori et al.*, 2003; *Kreidenweis et al.*, 2006), the CCN activation of small ($d_m < 150$ nm), dry slightly soluble organic particles is governed by the deliquescence of the particles (where $S_{del} >$ calculated S_c), and CCN activation follows the deliquescence curve for the particles. For larger dry particles, where $S_{del} <$ calculated S_c , CCN activation follows the Köhler curve. As expected, 'wet' adipic acid particles activate at the supersaturations predicted by Köhler theory for all sizes measured in this study (70-200 nm).

A solvent-independent method for generating pure organic particles (via homogeneous nucleation) was used for this study and found to provide results that were more reproducible than those obtained in our experiments as well as previously published experiments with particles produced by atomizing solutions. The homogeneously nucleated particles were measured to be nearly spherical ($\chi \le 1.2$). These results suggest that the observed scatter in the published literature for the CCN activity of adipic acid particles may be related to either the impurities in the solvents used or the inadvertent formation of non-spherical particles.

5.4.3 Soot Particle CCN Studies

As discussed in Chapter 4, soot particles are emitted directly into the atmosphere as a product of incomplete combustion of fossil fuels. Soot particles are initially hydrophobic and CCN inactive. As the need for a better understanding of CCN processes has risen, the role of soot particles in cloud formation has gained much interest (*Andreae and Rosenfeld*, 2008; *Baumgardner et al.*, 2004; *Dusek et al.*, 2006; *Bond*, 2007; Zuberi et al., 2005). Specifically, this interest is driven by the potential optical effect that soot nuclei could have on the albedo of a cloud (*Ramanathan and Carmichael*, 2008; *Mikhailov et al.*, 2006). It is possible for soot particles to act as CCN if they become coated with water-soluble species as a result of atmospheric processing during their residence time in the atmosphere (*Cross et al.*, 2008). To measure the influence of soot particle CCN activation, three different soot systems were studied: Soot coated with slightly soluble adipic acid, soot coated with sulfuric acid, and soot oxidized in the presence of ozone (O_3) and hydroxyl radicals (OH). Results from the three different soot activations.

5.4.3.1 Nascent uncoated soot

Before showing the change in CCN activation of coated soot particles it is necessary to illustrate the CCN inactivity of the nascent soot particles generated with our apparatus. At a supersaturation of 3.7% (the maximum possible in the CCNC instrument used here) zero CCN activation was observed for 250 nm soot particles produced at an equivalence ratio of 5.0. Smaller particle sizes and lower fuel-to-air equivalence ratios showed the same result. The nascent soot particles do not activate to form cloud droplets.

5.4.3.2 Soot Coated with Adipic Acid

In this set of coating experiments, four soot particles, $d_{core} = 88$ nm, 102 nm, 136 nm and 181 nm, were coated with adipic acid. The CCN activity of the soot coated with adipic acid was measured as a function of the adipic acid coating thickness (< 3 – 75 nm).

Figure 5-13 shows the measured critical supersaturations as a function of the total particle diameter (soot core + adipic acid coating). Our CCN activation measurements for dry adipic acid particles are included for comparison.



Figure 5-13: S_c plotted as a function of the total particle diameter (soot core + adipic acid coating) for adipic acid coated soot particles of sizes $d_{core} = 88$ nm (diamonds), 102 nm (squares), 136 nm (triangles), and 181 nm (circles). Also included are the results for dry adipic acid obtained in this study (blue).

The points at the top of each activation line are soot particles coated with very thin layers (< 3nm) of adipic acid. These data points indicate that a very small layer of adipic acid on a CCN-inactive particle triggers CCN activation near (or above) the calculated critical supersaturations of a wettable solid core (the black line in Figure 5-13).

The measured critical supersaturations for adipic acid coatings on smaller soot core sizes ($d_{core} = 88$ nm and 102 nm) approach the critical supersaturations measured for dry adipic acid. The particles activate at the deliquescence relative humidity DRH, or S_{del} of adipic acid (See section 5.2.3). This observation suggests that the soot core acts as a scaffold for the adipic acid coating and deliquescence is determined by the total particle diameter. The soot-adipic acid particle acts as a pure adipic acid particle during CCN activation because the adipic acid completely coats the soot core. Here, the total size of the particle (and not the composition) governs CCN activation.

The S_c measurements for the larger soot core sizes ($d_{core} = 136$ and 181 nm) are displaced to the right of the dry adipic acid line. This indicates that the larger soot core sizes coated with adipic acid do not activate according to either the deliquescence or the standard Köhler theory for adipic acid. This observation seems to suggest that for these types of particles, the soot core does not simply act as a scaffold for the adipic acid coating. It appears that from the perspective of CCN activation, the effective diameter of the larger soot particles coated with adipic acid is less than the measured particle diameter. Since the soot itself is hydrophobic, water interacts only with the adipic acid coated onto the soot. Therefore, only the diameter of the adipic acid coating influences the CCN activity of the coated particle (producing an effective diameter). It is possible that the smaller soot cores are coated more thoroughly than the larger cores. A full coating yields an effective diameter equal to the total particle diameter. On the other hand, a partial coating may produce adipic acid "islands" with an effective diameter that is smaller than the total particle diameter. Other mechanisms related to shape and fractality factors could be suggested to explain the difference between small and large soot core sizes coated with adipic acid and thus, the S_c measurements for the larger soot particles require further investigation.

5.4.3.3 Soot Particles Coated with Sulfuric Acid (H₂SO₄)

As part of the black carbon intercomparison study summarized in Chapter 6, the CCN activity of fractal soot particles coated with H₂SO₄ was measured. In contrast to the adipic acid-coated soot particles discussed in the previous section, in this case fractal soot cores of $d_m = 53$, 207, and 209 nm were used. The $d_m = 53$ nm soot core was coated to dm of 117 nm with H₂SO₄. The original soot particle was CCN inactive whereas the coated soot particle activated at an $S_c = 0.224\%$. This data point is shown as the open square in Figure 5-14.

The $d_m = 209$ nm soot core was coated with two different amounts of H₂SO₄. The initial coating resulted in a dm = 209, but this does not mean that H₂SO₄ was not coating the particle. In the case of fractal particles, one must consider that the reported d_m is a measure of the major axis of the particle. As the H₂SO₄ begins to coat the fractal soot, it must first fill the void space within the fractal structure. Therefore, it is possible to measure $d_m = 209$ nm and still have a significant fraction of H₂SO₄ on the particle. The chemical composition of the coated particle as measured by the LS-ToF-AMS confirms the presence of H₂SO₄ on the particles. The 209 nm soot core was also coated to a dm = 217 nm. Both data points are shown in Figure 5-14 as solid squares. The third set of

H₂SO₄ coated soot particles started with a fractal core of 207 nm and coated the particle to dm = 225, 233, 250, and 275 nm. The 275 nm core activated below the minimum S_c value of the CCNC, so a data point was not obtained in this case. For the three other cases, as expected, the coated particles activated at successively lower supersaturations as the coating thickness of H₂SO₄ increased. These data points are shown as solid circles in Figure 5-14.



Figure 5-14: S_c plotted versus coated particle diameter for three different size soot cores coated with H₂SO₄ (See text for details).

The CCN experiments with H₂SO₄ coated soot particles during the black carbon intercomparison study were limited by the time required to complete a full CCN activation curve. As a result, only a few coated particle systems were analyzed. The results show that H_2SO_4 coatings readily induce CCN activation on otherwise inactive of fractal soot cores. More detailed studies of the CCN activation of H_2SO_4 coated soot particles are currently underway.

5.4.3.4 CCN Activity of Oxidized Soot Particles with the Potential Aerosol Mass (PAM) Instrument

In addition to changes in CCN activity due to coatings, soot particles also undergo oxidation reactions in the atmosphere that can dramatically influence the CCN activity of the particles. To gain insight into the CCN activity of oxidized soot, size selected fractal soot particles ($d_m = 163$ nm) were exposed to varying amounts of hydroxyl radical (OH) – produced by the photolysis of water vapor by UV. For this experiment the particle generation and analysis techniques described previously were combined with a new aerosol processing chamber call the Potential Aerosol Mass instrument (PAM) (*Kang et al.*, 2007). The size-selected soot particles are passed through the PAM chamber, exposed to high OH concentrations and then sampled with the analysis instrumentation CCNC-SMPS-AMS. The high OH concentrations are meant to simulate long atmospheric residence times (i.e. days of atmospheric processing). In this way, the PAM chamber creates a fast laboratory-based method for characterizing heavily processed aerosol particles.

The results of the oxidized soot CCN study are slightly different from those of the coated soot CCN studies. In this case, the size of the particles does not change with increasing oxidation and therefore, to plot critical supersatuation as a function of dry particle size is not particularly helpful. Instead, in Figure 5-15 we show the CCN

activation curves (CCN/CPC) for the different OH concentrations studied. Each curve is plotted with respect to the supersaturation in the CCNC column.



Figure 5-15: CCN activation curves (CCN/CPC) as a function of supersaturation for 163 nm soot particles exposed to increasing concentrations of OH and O_3 within the Potential Aerosol Mass (PAM) instrument.

The data show that with increased OH concentration, the CCN activation of the 163 nm fractal soot particles increases. The results indicate, that with residence times of a few days in the atmosphere, soot particle exposure to OH will readily activate to cloud droplets. Although the results from the PAM study are preliminary, they do present a solid basis for performing future CCN studies of oxidized soot particles.

5.4.3.5 Conclusions to CCN activation studies of soot particles

Three different CCN-soot particle studies were presented: Soot +adipic acid, soot+H₂SO₄, and soot+OH. An adipic acid coating on hydrophobic CCN-inactive soot particle yields a CCN active particle at atmospherically relevant supersaturations. For relatively small soot cores ($d_{core} = 88$ nm and 102 nm), the CCN activity of the coated particles approaches the deliquescence line of adipic acid. This suggests that for coated soot particles in this range of diameters, the total size of the particle determines CCN activation and the soot core acts as a scaffold for the deposition of adipic acid vapor. It appears that the CCN activation of larger coated soot cores occurs at higher supersaturations than is predicted by the deliquescence curve. It is hypothesized that larger soot particles are only partially coated with adipic acid, causing the mixed particles to be chemical composition dependent, and not total particle size dependent as observed for small soot core sizes.

Fractal soot particles coated with H_2SO_4 during the black carbon intercomparison study showed increasing CCN activity with increasing H_2SO_4 content. Soot particles with the thickest coatings approached the Köhler theory line for ammonium sulfate activation.

Fractal soot particles exposed to varying OH concentrations showed increased CCN activity with increasing OH exposure. The study indicates that oxidation reactions on the surface of the soot particles are important when considering the transformation in CCN activity of aged soot particles in the atmosphere.

5.5 SUMMARY

The indirect effect of aerosol particles (i.e. particles forming cloud droplets) on climate contributes the largest uncertainty of any single component of the Earthatmosphere system, to current projections of man-made climate change. This chapter presented results from a series of laboratory experiments designed to examine the influence of particle shape, size, and chemical composition (solubility) on CCN activity. Three different particle types, spanning a wide range of water solubility, were studied including ammonium sulfate, adipic acid, and soot. For each system, nascent and coated particles were tested to determine how the CCN activity of the particles changed as they undergo potential scenarios of atmospheric processing. The CCN activity of ammonium sulfate particles was found to be highly dependent on the composition, thickness, and phase of the coating material used. When coated with a solid, insoluble organic (stearic acid) the CCN activity of the ammonium sulfate core was shut down. For cases of slightly soluble solid (adipic acid) and insoluble liquids (oleic acid and DOS), the CCN response of the coated ammonium sulfate particles was effectively modeled with modified Köhler theory.

The CCN activity of slightly soluble adipic acid was examined in detail in the context of nearly all previously published results for adipic acid CCN activation. Insights into the DRH dependence of CCN activity for dry adipic acid particles and a novel method for production of 'wet' adipic acid particles were provided. Experiments with adipic acid-coated soot particles revealed that fractal, non-activating soot cores act as a scaffold under conditions of sufficient adipic acid coating. Under these conditions, the activation of the coated particles follows the activation trend for dry adipic acid.

Preliminary results from the black carbon intercomparison study at Boston College were presented that showed the influence of H_2SO_4 on the CCN activation of hydrophobic fractal soot cores.

Preliminary results from oxidation experiments using the PAM instrument were also presented and showed that with increasing concentrations of OH and O3, soot particle activated at progressively lower S_c values.

5.6 APPENDIX 5A: CCN Instrument Calibration

To perform reliable CCN activation measurements requires an accurate knowledge of the relationship between the temperature difference dT along the CCNC column and the supersaturation *S*. This relationship is determined by calibration, using a well-characterized highly soluble inorganic salt, such as $(NH_4)_2SO_4$ or NaCl. Previous studies have reported a linear relationship between instrument dT and *S* at a flow rate of 0.5 L/min for dT > 3 K (*Roberts and Nenes*, 2005). For smaller dT the relationship becomes nonlinear (*Rose et al.*, 2007). In order to obtain a larger range of supersaturations, we operate the instrument at a higher flow rate up to 1.0 L/min. We calibrated the CCN instrument at higher flow rates between 0.5 L/min and 1 L/min.

The calibration arrangement is similar to that shown in Figure 5-4. Calibration was done with ammonium sulfate aerosol particles generated by atomization of an aqueous solution of $(NH_4)_2SO_4$. The particles were dried to a relative humidity (RH) < 10% by passing the aerosol flow through diffusion driers. A narrow monodisperse size distribution $(d_m \pm 10\%)$ was obtained by passing the particles through two Differential

Mobility Analyzers (DMA I and DMA II). The aerosol flow was divided between the CCNC instrument and the condensation particle counter (CPC). Note that the CCNC counts the number of activated particles, while the CPC counts the total number of particles in the flow.

The following method was used to calibrate the CCNC instrument. Ammonium sulfate particles of a specific size (d_m) flowed into the CCNC and CPC instruments. At a set value of dT both the CCNC and the CPC particle counts were recorded. The value of dT was systematically varied. Equilibration time between dT settings was about 1 min. The value of the critical dT (dT_c) was recorded. (dT_c is the temperature difference at which 50% of the particles are activated.) Alternately, dT can be kept constant while the particle diameter is systematically varied. Again, the dT_c and the corresponding particle size are recorded. The two methods yield similar results. The critical supersaturation (S_c) was calculated for each particle size using standard Köhler theory. In this way, S_c vs dT_c calibration plots for the CCNC instrument are obtained.

The results of calibrations for flow rates of 0.93 L/min and 1 L/min are shown in Figures 5A-1 and 5A-2. These were the two flow rates used in our experiments. The nonlinear part of the curve was fitted to a power function:

$$S_{c,0} = y_0 + A \cdot dT^x \tag{5A-1}$$

Here, $S_{c,0}$, A and x are parameters determined by the fit.



Figure 5A-1: Calculated critical supersaturation as a function of CCN instrument dT. The instrument flow rate was 0.93 L/min.



Figure 5A-2: Calculated critical supersaturation as a function of CCN instrument dT. The instrument flow rate was 1 L/min.

The calibration curves at both flow rates are nonlinear for dT < 5 K. In fact, over the range of flow rates studied, the transition into the nonlinear region is unchanged at dT< 5 K. As was stated, some earlier measurements found the nonlinear portion of the calibration curve for dT < 3 K, implying that the calibration is instrument specific.

While the transition to the nonlinear portion of the calibration curve is independent of the flow rate, the slopes of the linear part of the curve are a sensitive function of the flow rate as is evident in the figures. For a flow rate of 0.93 L/min the slope is 0.106 %/K, for a flow rate of 1 L/min it is 0.149 %/K. In the time period of the CCN experiments (~ 8 months) the calibration was periodically repeated and was found to remain constant.

5.7 REFERENCES FOR CHAPTER V

- Andreae, M.O. & Rosenfeld, D. 2008, "Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols", *Earth-Science Reviews*, vol. 89, no. 1-2, pp. 13-41.
- Baumgardner, D., Raga, G.B. & Muhlia, A. 2004, "Evidence for the formation of CCN by photochemical processes in Mexico City", *Atmospheric Environment*, vol. 38, no. 3, pp. 357-367.
- Bilde, M. & Svenningsson, B. 2004, "CCN activation of slightly soluble organics: the importance of small amounts of inorganic salt and particle phase", *Tellus Series B-Chemical and Physical Meteorology*, vol. 56, no. 2, pp. 128-134.
- Bond, T.C. 2007, "Can warming particles enter global climate discussions?", *Environmental Research Letters*, vol. 2, no. 4.
- Broekhuizen, K., Kumar, P.P. & Abbatt, J.P.D. 2004, "Partially soluble organics as cloud condensation nuclei: Role of trace soluble and surface active species", *Geophysical Research Letters*, vol. 31, no. 1.

- Corrigan, C.E. & Novakov, T. 1999, "Cloud condensation nucleus activity of organic compounds: a laboratory study", *Atmospheric Environment*, vol. 33, no. 17, pp. 2661-2668.
- Cross, E.S., Onasch, T.B., Canagaratna, M., Jayne, J.T., Kimmel, J., Yu, X.Y., Alexander, M.L., Worsnop, D.R. & and Davidovits, P. 2008, "Single Particle Characterization Using a Light Scattering Module Coupled to a Time-of Flight Aerosol Mass Spectrometer", *Submitted to ACPD*, .
- Cross, E.S., Onasch, T.B., Wrobel, W., Ahern, A., Jayne, J.T., Trimborn, A., Cappa, C., Schwarz, J., Lack, D., Olfert, J., Slowik, J., Massoli, P., Spackman, R., Brem, B., Worsnop, D.R. & and Davidovits, P. 2008, "Overview of the 2nd Boston College/Aerodyne Black Carbon Intercomparison Study", *In Preparation for ACPD*,
- Cruz, C.N. & Pandis, S.N. 1997, "A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei", *Atmospheric Environment*, vol. 31, no. 15, pp. 2205-2214.
- DeCarlo, P.F., Slowik, J.G., Worsnop, D.R., Davidovits, P. & Jimenez, J.L. 2004, "Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory", *Aerosol Science and Technology*, vol. 38, no. 12, pp. 1185-1205.
- Dinar, E., Anttila, T. & Rudich, Y. 2008, "CCN activity and hygroscopic growth of organic aerosols following reactive uptake of ammonia", *Environmental science & technology*, vol. 42, no. 3, pp. 793-799.
- Dusek, U., Reischl, G.P. & Hitzenberger, R. 2006, "CCN activation of pure and coated carbon black particles", *Environmental science & technology*, vol. 40, no. 4, pp. 1223-1230.
- Facchini, M.C., Decesari, S., Mircea, M., Fuzzi, S. & Loglio, G. 2000, "Surface tension of atmospheric wet aerosol and cloud/fog droplets in relation to their organic carbon content and chemical composition", *Atmospheric Environment*, vol. 34, no. 28, pp. 4853-4857.
- Hartz, K.E.H., Tischuk, J.E., Chan, M.N., Chan, C.K., Donahue, N.M. & Pandis, S.N. 2006, "Cloud condensation nuclei activation of limited solubility organic aerosol", *Atmospheric Environment*, vol. 40, no. 4, pp. 605-617.
- Henning, S., Rosenorn, T., D'Anna, B., Gola, A.A., Svenningsson, B. & Bilde, M. 2005, "Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt", *Atmospheric Chemistry and Physics*, vol. 5, pp. 575-582.
- Hori, M., Ohta, S., Murao, N. & Yamagata, S. 2003, "Activation capability of water soluble organic substances as CCN", *Journal of Aerosol Science*, vol. 34, no. 4, pp. 419-448.
- Kang, E., Root, M.J., Toohey, D.W. & Brune, W.H. 2007, "Introducing the concept of Potential Aerosol Mass (PAM)", *Atmospheric Chemistry and Physics*, vol. 7, no. 22, pp. 5727-5744.
- Kreidenweis, S.M., Petters, M.D. & DeMott, P.J. 2006, "Deliquescence-controlled activation of organic aerosols", *Geophysical Research Letters*, vol. 33, no. 6.
- Prenni, A.J., DeMott, P.J., Kreidenweis, S.M., Sherman, D.E., Russell, L.M. & Ming, Y. 2001, "The effects of low molecular weight dicarboxylic acids on cloud formation", *Journal of Physical Chemistry A*, vol. 105, no. 50, pp. 11240-11248.
- Pruppacher, H.R. & Klett, J.D. 1997, *Microphysics of Clouds and Precipitation: An Introduction to Cloud Chemistry and Cloud Electricity*, Springer.
- Ramanathan, V. & Carmichael, G. 2008, "Global and regional climate changes due to black carbon", *Nature Geoscience*, vol. 1, no. 4, pp. 221-227.
- Raymond, T.M. & Pandis, S.N. 2002, "Cloud activation of single-component organic aerosol particles", *Journal of Geophysical Research-Atmospheres*, vol. 107, no. D24.
- Rissman, T.A., Varutbangkul, V., Surratt, J.D., Topping, D.O., McFiggans, G., Flagan, R.C. & Seinfeld, J.H. 2007, "Cloud condensation nucleus (CCN) behavior of organic aerosol particles generated by atomization of water and methanol solutions", *Atmospheric Chemistry and Physics*, vol. 7, no. 11, pp. 2949-2971.
- Roberts, G.C. & Nenes, A. 2005, "A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements", *Aerosol Science and Technology*, vol. 39, no. 3, pp. 206-221.

- Rose, D., Gunthe, S.S., Mikhailov, E., Frank, G.P., Dusek, U., Andreae, M.O. & Poschl, U. 2008, "Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment", *Atmospheric Chemistry and Physics*, vol. 8, no. 5, pp. 1153-1179.
- Schwartz, S.E., Charlson, R.J. & Rodhe, H. 2007, "Quantifying climate change too rosy a picture?", *Nature Reports Climate Change*, vol. 1, pp. 23-24.
- Shulman, M.L., Jacobson, M.C., Carlson, R.J., Synovec, R.E. & Young, T.E. 1996, "Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets", *Geophysical Research Letters*, vol. 23, no. 3, pp. 277-280.
- Slowik, J.G. 2006, Morphology, Composition, and Atmospheric Processing of Soot Particles, Boston College.
- Slowik, J.G., Cross, E.S., Han, J.H., Davidovits, P., Onasch, T.B., Jayne, J.T., WilliamS, L.R., Canagaratna, M.R., Worsnop, D.R., Chakrabarty, R.K., Moosmuller, H., Arnott, W.P., Schwarz, J.P., Gao, R.S., Fahey, D.W., Kok, G.L. & Petzold, A. 2007, "An inter-comparison of instruments measuring black carbon content of soot particles", *Aerosol Science and Technology*, vol. 41, no. 3, pp. 295-314.
- Slowik, J.G., Cross, E.S., Han, J.H., Kolucki, J., Davidovits, P., Williams, L.R., Onasch, T.B., Jayne, J.T., Kolb, C.E. & Worsnop, D.R. 2007, "Measurements of morphology changes of fractal soot particles using coating and denuding experiments: Implications for optical absorption and atmospheric lifetime", *Aerosol Science and Technology*, vol. 41, no. 8, pp. 734-750.
- Solomon, S., Qin, D., Manning, M., Marquis, M., Averyt, K., Tignor, M. & and Miller, H.L.(. 2007, *IPCC: Climate change 2007: The Scientific Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Wrobel, W. 2008, *Exploring the Role of Particulate Matter in Global Warming*, Boston College.

Zuberi, B., Johnson, K.S., Aleks, G.K., Molina, L.T. & Laskin, A. 2005, "Hydrophilic properties of aged soot", *Geophysical Research Letters*, vol. 32, no. 1.

CHAPTER VI

INTERCOMPARISON STUDY OF BLACK CARBON INSTRUMENTS

JULY 2008

6.1 OVERVIEW

In July of 2008, the 2^{nd} intercomparison study of black carbon instruments at Boston College (BC²) was conducted. This was a follow-on experiment to the 1^{st} intercomparison study conducted in May 2005 (*Slowik, Cross et al.,* 2007a). In this chapter, lessons learned from the 1^{st} intercomparison are reviewed, improvements to the laboratory soot generation-sampling apparatus are described in greater detail, and the objectives, accomplishments, and preliminary results from the BC² study are presented.

The material presented in this chapter is being prepared for submission to *Atmospheric Chemistry and Physics Discussions* as Cross, E.S., Onasch, T.B., Wrobel, W., Ahern, A., Jayne, J.T., Trimborn, A., Cappa, C., Schwarz, J., Lack, D., Olfert, J., Slowik, J., Massoli, P., Spackman, R., Brem, B., Worsnop, D.R. & and Davidovits, P. 2008, "Overview of the 2nd Boston College/Aerodyne Black Carbon Intercomparison Study".

6.2 LESSONS LEARNED FROM 1st INTERCOMPARISON STUDY

During the 1st intercomparison study of black carbon instruments at Boston College, size-selected fractal soot particles ($d_m = 150 - 460$ nm) were produced at fuel-toair equivalence ratios of 2.3 and 3.5. Four mass-based measurement techniques were compared: a Multi-Angle Absorption Photometer (MAAP), Photoacoustic Spectrometer (PAS), Single Particle Soot Photometer (SP2), and the SMPS-AMS combination. In addition, Scanning Electron Microscope (SEM) filters were obtained for off-line microscopic analysis of particle shape (*Chakrabarty et al.*, 2007). Mass measurements were compared for nascent soot particles as well as soot particles coated with liquid (oleic acid) and solid (anthracene) organics (*Slowik, Cross et al.*, 2007b).

Results from the 1st intercomparison study have been reported (e.g. *Schwarz, Gao et al.*, 2006; *Gao, Schwarz et al.*, 2007; *Slowik, Cross et al.*, 2007a; *Chakrabarty et al.*, 2007). Here, we review the lessons learned from the 1st intercomparison and discuss the improvements made to the soot generation-sampling apparatus prior to the 2nd intercomparison study.

The main challenge of the 1st intercomparison study was the broad polydisperse size distribution of soot particles. As a result, multiply charged particles were transmitted through the DMA complicating the analysis of soot particles of a single d_m size. The two factors that lead to the broad polydisperse soot distributions were (1) the alignment and positioning of the sampling inlet with respect to the burner surface, and (2) the pre-mix and sampling flow rates of the soot generation-sampling system.

During the 1st intercomparison, the orientation of the sampling tip, with respect to the flame was set at a sampling height of ~ 18" (distance between the burner surface and the edge of the sampling tip). The sampling tip was purposely off-axis, with respect to the sooting center of the flame, to prevent rapid clogging of the inlet. Typically, the flame was operated continuously for 10-15 hours/day. At the end of each day, the sampling inlet was removed, cleaned, and re-installed. Care was taken throughout the experiments to re-configure the sampling apparatus in a reproducible fashion, but the soot generation-sampling system was not locked in position, resulting in variability in the day-to-day alignment of the system.

To minimize the influence of multiply charged particles, soot particles were doubly size-selected. The second DMA size-selected the doubly charged particles transmitted by the first DMA. Due to transmission efficiency losses within each DMA, particle number concentrations were often low, further complicating the experiments. Despite the challenge of low soot concentrations and instability in the soot generation-sampling interface, the 1st intercomparison study was able to successfully compare the response of the four different instruments to the mass of black carbon in the particles under a range of different experimental conditions (*Slowik, Cross et al.*, 2007a).

6.3 PREPARATION FOR 2ND INTERCOMPARISON STUDY (BC²)

As stated in Chapter 2, the first improvement made to the soot generationsampling apparatus was securing the flame base and sampling inlet with a stainless steal frame and mounting the apparatus to an optical table. As a result, reproducible alignment of the sampling inlet with the soot source was possible

In order to optimize the positioning of the sampling inlet with respect to the burner surface, an x-y-z translation stage was attached to the base of the burner. With this additional alignment control, the width and peak position of the polydisperse soot distribution was optimized so that monodisperse distributions of soot could be obtained with minimal influence from multiply charged particles. Figure 6-2 shows a schematic of the apparatus. Through characterization experiments, the optimal sampling height (distance between the burner surface and sampling inlet) was found to be ~ 10" (*Wrobel*,

2008). During the 1st intercomparison study, the sampling height was 18" with no control over the x-y-z alignment of the sampling tip.



Figure 6-1: Improved soot generation-sampling system apparatus with alignment controls. Stainless steel support structure not shown.

The sensitivity of the instruments studied vary. Therefore, each instrument requires a particle number concentration in a specific range for accurate measurement. The intercomparison studies conducted at Boston College included instruments that measured single particle properties and instruments that measured ensemble average properties. Typically, instruments that measure ensemble average properties require number concentrations of ~ 10,000-50,000 p/cm³ while single particle instruments are most effective at concentrations of ~ 500-3,000 p/cm³. Therefore, careful control of the number concentration of soot particles is essential to the success of any intercomparison study.

As shown in the inset of Figure 6-1, a flow of $N_{2 (g)}$ (called 'dilution N_2 flow') is introduced around the sampling tip to prevent soot from clogging the inlet. The dilution N_2 flow can be used to either concentrate or dilute the soot particles, depending on the desired conditions. Prior to the 2nd intercomparison study, the relationship between the N_2 sample flow and total particle concentration was characterized for a range of soot conditions. By systematically varying the dilution N_2 flow in the soot system, soot number concentrations were obtained across the desired range.

All input flows to the soot source were carefully tested to maximize the stability of the system for each soot condition specified in the proposed experimental matrix for the BC^2 study.

The final modification to the soot generation-sampling system was the integration of a diaphragm pump after DMA I. In the first intercomparison study, the particle flow rate (~ 3 L/min) was determined by the total flow required from the combination of instruments downstream. For the BC² study, much higher flow rates were required by the suite of instruments studied. As a result, a dilution mechanism was designed to introduce extra N₂ flow downstream of the particle size selection. This arrangement also allowed for humidification of the extra N₂ flow and subsequent relative humidity (RH) control in the system. The diaphragm pump was used to produce a flow rate of ~ 2 L/min through the DMA apparatus, keeping the size resolution of the DMA high (~10:1 Sheath:Mono), \pm 10% of the mode diameter. The extra N₂ flow compensated the particle flow so that each instrument could sample at its nominal flow rate. The total flow of the system with all instruments attached to the sampling line was ~ 22 L/min.

Through optimization of the critical flow rates of the soot generation-sampling interface as well an improved control of the alignment of the sampling tip, stable and reproducible distributions of soot particles were obtained during the BC^2 study. Reconfiguration of the flow control through the system, allowed simultaneously measurement of the soot particles with as many as 18 instruments.

6.4 SUMMARY OF 2ND INTERCOMPARISON STUDY (BC²)

The BC² project was conducted from July 7 – 26, 2008 in the Davidovits laboratory at Boston College. Altogether 18 instruments participated in the study; 8 mass-based, 8 optically-based and 2 filter samples. (As compared to five instruments in the 1st intercomparison study.) Twenty-six people representing 12 institutions participated in the project. The instruments and participants in the study are listed in Table 6-1.

Achim Trimborn	Aerodyne Research Inc. (ARI)
Adam Ahern	Boston College (BC)
Andy Freedman	ARI
Arthur Sedlacek	Brookhaven National Laboratory (BNL)
Benjamin Brem	University of Illinois (Tami Bond group)
Billy Wrobel	BC
Christopher Cappa	UC Davis
Claudio Mazzoleni	Los Alamos National Laboratory (LANL)
Daniel Lack	NOAA CIRES
Doug Worsnop	ARI
Dwight Thornhill	Virginia Tech (Linsey Marr group)
Eben Cross	BC
Greg Kok	Droplet Measurement Technologies (DMT)
Jason Olfert	BNL
Jay Slowik	University of Toronto
John Jayne	ARI
Joshua (Shuka) Schwarz	NOAA CIRES
Leah Williams	ARI
Mavendra Dubey	LANL
Paola Massoli	NOAA ESRL
Paul Davidovits	BC
R. (Subu) Subramanian	DMT
Ryan Spackman	NOAA ESRL
Sally Ng	ARI
Steffen Freitag	University of Hawaii (Tony Clarke group)
Tim Onasch	ARI

Table 6-1. List of scientists and their institutional affiliations that participated in the BC^2 study.

6.4.1. Instruments Studied during the 2nd Intercomparison

Particle generation and conditioning equipment

• Premixed flat flame burner

- Coating and humidity conditioners
- Thermal Denuder (TD; Aerodyne Research)
- Differential Mobility Analyzers (DMA; TSI model 3076 and 3080) two in number
- Assorted flow meters, flow controllers and humidity monitors

Filters samples

- Organic Carbon-Elemental Carbon Analyzer (OCEC; Sunset Labs) filter samples
- Scanning Electron Microscope (SEM) filter samples

Mass-based instruments

- Scanning Mobility Particle Sizer (SMPS; TSI)
- Condensation Particle Counters (CPC; TSI model 3022a) two in number
- Time of Flight Aerosol Mass Spectrometer (TOF-AMS; Aerodyne Research)
- Soot Particle Soot Photometer Aerosol Mass Spectrometer (SP2-AMS; Aerodyne Research)
- Single Particle Soot Photometer (SP2; Droplet Measurement Technology) three in number
- Couette Centrifugal Particle Mass Analyzer (CPMA) and CPC (TSI model 3025)
- Particle-Bound Polycyclic Aromatic Hydrocarbons (PAH) Monitor (PAS2000CE; EcoChem)
- Diffusion Charger (DC2000CE; EcoChem)
- Cloud Condensation Nuclei Counter (CCN; DMT)

Optically-based instruments

•	Photo-acoustic Spectrometer (PAS; NOAA)	$\lambda = 532 \text{ nm}$
•	Photo-acoustic Soot Spectrometer (PASS-3; DMT)	$\lambda = 405, 532$
	and 781 nm	
•	Photo-Thermal Interferometer (PTI)	$\lambda = 532 \text{ nm}$
•	Cavity-Ring Down (CRD) Extinction Spectrometer	$\lambda = 355, 532$
	and 1064 nm	
•	Cavity Attenuated Phase Shift (CAPS) Extinction monitor	$\lambda = 440 \text{ nm}$
•	Particle Soot Absorption Photometer (PSAP; Radiance Res.)	$\lambda = 450, 550$
	and 700 nm	
•	Nephelometer (TSI model 3563)	$\lambda = 450, 550$
	and 700 nm	
•	Multi-Angle Absorption Photometer (MAAP; Thermoelectron)	$\lambda = 670 \text{ nm}$

Figure 6.2 shows the range of wavelengths covered by the instruments used during the BC^2 study with respect to the amount of circumsolar radiance (in Watts/m²) at each respective wavelength.



Figure 6.2: Range of wavelengths covered with optical measurements used during the BC^2 study. The direct circumsolar radiance in W/m^2 is plotted as a function of wavelength in the lower panel.

6.4.2. Experimental Objectives and Highlights

Over course of the three weeks, 318 runs were performed covering a matrix that systematically tested the performance of each instrument over a range of relevant parameters. Opportunity was provided for each instrument to sample soot particles as a function of the following measured (directly or indirectly) and controlled parameters: particle mobility size ($30 \le d_m \le 300$ nm), particle number concentration (500-50,000 p/cc), particle shape (dynamic shape factor and fractal dimension), particle chemistry and density (changed via coatings), black carbon mass, and relative humidity (5-90%). In selected runs, particles were coated with a measured thickness ($1 \text{ nm} \le \Delta d_m \le 150$ nm) of

sulfuric acid (H_2SO_4) or dioctyl sebacate (DOS). In addition to flame-generated soot, black carbon (BC) particles were also obtained by atomizing fullerene soot, glassy carbon spheres, oxidized flame soot, Regal black toner, and Aquadag paint.



Figure 6.3: Schematic of the sampling configuration during the BC^2 intercomparison study.

The science goals for the project were organized into one set of objectives for the mass-based measurements and another set of objectives for the optical-based measurements. These goals are listed below including key questions potentially addressed through the BC^2 study. A schematic of the instrument configuration is shown in Figure 6-3.

Mass-based Measurement Goals:

- Use the Couette Centrifugal Particle Mass Analyzer (CPMA) to measure absolute particle mass and accurately determine the particle density and fractal dimension. Compare these measurements the results obtained with the SMPS-AMS measurements of particle mass, density, and fractal dimension. Use the CPMA results as a reference for other elemental carbon mass measurements.
- 2. Quantify the Soot Particle Aerosol Mass Spectrometer (SP2AMS) carbon ion cluster measurements as a function of black carbon particle mass. Investigate how coatings (liquid/solid, organic/inorganic/water) affect carbon ion cluster measurements. How well can the SP2AMS characterize the chemistry and mass of the soot particle coatings?
- 3. Verify the quantification of Soot Particle Soot Photometer (SP2) incandescence measurements as a function of black carbon particle mass. Investigate how coatings (liquid/solid, organic/inorganic/water) affect the SP2 measurements.
- 4. Determine how DMA-CPMA, SP2AMS, and SP2 black carbon mass measurements compare with OC/EC mass measurements. Investigate how coatings (liquid/solid, organic/inorganic/water) affect the OC/EC measurement. In particular, how well can the OC/EC instrument separate elemental carbon from organic carbon?

Optical-based Measurement Goals:

- Measure the mass specific absorption coefficients as a function of black carbon particle type (e.g. as function of fuel, fuel-to-air ratio, size) and coatings (liquid/solid, organic/inorganic/water).
- 6. Determine how water coatings (e.g. RH) affect optical signals within the Photoacoustic Spectrometer (PAS), the Particle Soot Absorption Photometer (PSAP), and the Multi-Angle Absorption Photometer (MAAP). Particles may rearrange or collapse during denuding of coating material. Determine how morphology changes affect optical signals.
- 7. Determine the effects of absorbing organics on black carbon particles.
- 8. Complete an optical closure study (Extinction, Scattering, and Absorption) by utilizing the extinction and scattering measurements made with the new Aerodyne Cavity Attenuated Phase Shift (CAPS) instrument, the NOAA Cavity Ring-Down (CRD) extinction system, and the various absorption and scattering instruments.

6.4.3. Highlights from BC²

While the final project evaluation will not be available until the data analysis is completed, the goals have been met and in some cases exceeded. An overview paper featuring the main results from the BC^2 intercomparison study is in progress (*Cross et al.*, 2008). Some of the highlights that will be featured in the overview paper are listed below:

#		Science Goals
	Highlights	Addressed
1	Particle shape determination as a function of fuel-to-air ratio and collapse observed due to coatings	1
2	Characterization of several new instruments currently under development	2, 3, 4
3	Characterization of the physical and chemical properties of various types of black carbon particles (including incandescence, fullerene content, surface-bound PAH, etc.)	3, 4
4	Mass specific absorption measurements as a function of fuel-to-air ratio and carbon particle type	5
5	Optical absorption enhancement measurements as a function of coatings	5
6	Wavelength-dependent measurements of absorption, scattering, and extinction as a function of fuel-to-air ratio, particle coating, and relative humidity	6, 7, 8

Table 6-2. Highlights from the BC^2 intercomparison study

6.5 REFERENCES

- Chakrabarty, R.K., Moosmuller, H., Arnott, W.P., Garro, M.A., Slowik, J.G., Cross, E.S., Han, J.H., Davidovits, P., Onasch, T.B. & Worsnop, D.R. 2007, "Light scattering and absorption by fractal-like carbonaceous chain aggregates: Comparison of theories and experiment", *Applied Optics*, vol. 46, no. 28, pp. 6990-7006.
- Cross, E.S., Onasch, T.B., Wrobel, W., Ahern, A., Jayne, J.T., Trimborn, A., Cappa, C., Schwarz, J., Lack, D., Olfert, J., Slowik, J., Massoli, P., Spackman, R., Brem, B., Worsnop, D.R. & and Davidovits, P. 2008, "Overview of the 2nd Boston College/Aerodyne Black Carbon Intercomparison Study", *In Preparation for ACPD*,
- Gao, R.S., Schwarz, J.P., Kelly, K.K., Fahey, D.W., Watts, L.A., Thompson, T.L., Spackman, J.R., Slowik, J.G., Cross, E.S., Han, J.H., Davidovits, P., Onasch, T.B. & Worsnop, D.R. 2007, "A novel method for estimating light-scattering properties of soot aerosols using a modified single-particle soot photometer", *Aerosol Science and Technology*, vol. 41, no. 2, pp. 125-135.

- Schwarz, J.P., Gao, R.S., Fahey, D.W., Thomson, D.S., Watts, L.A., Wilson, J.C., Reeves, J.M., Darbeheshti, M., Baumgardner, D.G., Kok, G.L., Chung, S.H., Schulz, M., Hendricks, J., Lauer, A., Karcher, B., Slowik, J.G., Rosenlof, K.H., Thompson, T.L., Langford, A.O., Loewenstein, M. & Aikin, K.C. 2006, "Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere", *Journal of Geophysical Research-Atmospheres*, vol. 111, no. D16.
- Slowik, J.G. 2006, Morphology, Composition, and Atmospheric Processing of Soot Particles, Boston College.
- Slowik, J.G., Cross, E.S., Han, J.H., Davidovits, P., Onasch, T.B., Jayne, J.T., WilliamS, L.R., Canagaratna, M.R., Worsnop, D.R., Chakrabarty, R.K., Moosmuller, H., Arnott, W.P., Schwarz, J.P., Gao, R.S., Fahey, D.W., Kok, G.L. & Petzold, A. 2007, "An inter-comparison of instruments measuring black carbon content of soot particles", *Aerosol Science and Technology*, vol. 41, no. 3, pp. 295-314.
- Slowik, J.G., Cross, E.S., Han, J.H., Kolucki, J., Davidovits, P., Williams, L.R., Onasch, T.B., Jayne, J.T., Kolb, C.E. & Worsnop, D.R. 2007, "Measurements of morphology changes of fractal soot particles using coating and denuding experiments: Implications for optical absorption and atmospheric lifetime", *Aerosol Science and Technology*, vol. 41, no. 8, pp. 734-750.
- Wrobel, W. 2008, *Exploring the Role of Particulate Matter in Global Warming*, Boston College.

APPENDIX TO THESIS

ABBREVIATIONS

AMS	Aerodyne Aerosol Mass Spectrometer
ARI	Aerodyne Research, Inc.
ATOFMS	Aerosol Time-of-Flight Mass Spectrometer
BBOA	Biomass Burning Organic Aerosol
BC	Black carbon
CAPS	Cavity Attenuated Phase Shift Extinction monitor
CCN	Cloud Condensation Nuclei
CCNC	Cloud Condensation Nuclei Counter
CPC	Condensation Particle Counter
СРМА	Couette Centrifugal Particle Mass Analyzer
CRD	Cavity-Ring Down Extinction Spectrometer
DC	Diffusion Charger
DMA	Differential Mobility Analyzer
DMT	Droplet Measurement Technologies
DOS	Dioctyl sebacate
EC	Elemental Carbon
GC	Glassy carbon
HOA	Hydrocarbon-like Organic Aerosol

IPCC	Inter-Governmental Panel on Climate Change
LOSU	Level of Scientific Understanding
LS-AMS	Light Scattering-AMS system with Quadrupole Mass Spectrometer
LS-ToF-AMS	Light Scattering AMS system with a Time-of-Flight Mass
	Spectrometer
LSSP	Light Scattering Single Particle Mode
LT	Local Time
OC	Organic carbon (non-refractory)
MAAP	Multi-Angle Absorption Photometer
MCMA-2006	Mexico City Metropolitan Area field study during March 2006
MILAGRO	Megacity Initiative: Local and Global Research Observations
MS	Mass Spectrum Mode
NEAQS	North East Air Quality Study
NOAA	National Oceanic and Atmospheric Administration
OOA	Oxygenated Organic Aerosol
РАН	Polyaromatic hydrocarbons
PALMS	Particle Analysis by Laser Mass Spectrometry
PAS	Photoacoustic Spectrometer
PASS-3	Photo-acoustic Soot Spectrometer
PAS2000CE	Particle-Bound Polycyclic Aromatic Hydrocarbons Monitor
PCA	Principle Component Analysis
PMF	Positive Matrix Factorization
PMT	Photomultiplier Tube

PSAP	Particle Soot Absorption Photometer
PTI	Photo-Thermal Interferometer
PTOF	Particle Time-of-Flight Mode
Q-AMS	AMS equipped with a Quadrupole mass spectrometer
RF	Radiative Forcing
RH	Relative humidity
RSMS	Rapid Single Particle Mass Spectrometer
SEM	Scanning Electron Microscope
SMPS	Scanning Mobility Particle Sizer
SP2	Single Particle Soot Photometer
SP2AMS	Single Particle Soot Photometer Aerosol Mass Spectrometer
SPLAT-MS	Single Particle Laser Ablation Time-of-flight Mass Spectrometer
TD	Thermal Denuder
TOF-AMS	Aerodyne Aerosol Mass Spectrometer with time-of-flight detector
TOFMS	Time-of-Flight Mass Spectrometer

SYMBOLS

d_p	physical diameter	
-------	-------------------	--

- d_m electrical mobility diameter
- *d*_o optical diameter
- d_a aerodynamic diameter
- d_{ca} aerodynamic diameter in the continuum regime
- d_{va} vacuum aerodynamic diameter

- d_{ve} volume equivalent diameter
- ρ_0 unit density
- ρ_p particle density
- ρ_m material density
- ρ_{eff} effective density
- ρ_{LS} Single particle density determined with LS-AMS
- ρ_{cc} chemical composition-based density
- R_{LS} scattered light intensity
- χ dynamic shape factor
- χ_t dynamic shape factor in continuum regime
- χ_v dynamic shape factor in free-molecular regime
- m_p mass of particle
- λ wavelength of laser light
- v_p particle velocity
- v_0 unit velocity
- *n* real or scattering component of the refractive index
- *k* imaginary or absorption component to the refractive index
- σ_{LS} standard deviation of scattered light signals
- σ_v particle beam width at the surface of the vaporizer
- σ_l particle beam width at the laser beam time-of-flight position
- σ_{laser} 1 σ scattering detection width of the laser beam
- R_p surface albedo

- $F_{s,i}$ flux densities of incoming solar radiation
- $F_{s,r}$ flux densities of reflected solar radiation
- F_l flux density of emitted longwave radiation