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Effects of Drying Rates on Size and Morphology of Nanoparticles

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EFFECTS OF DRYING RATES ON SIZE AND MORPHOLOGY OF NANOPARTICLES

by

Judy Phan

A Master's Thesis
Presented to the Faculty of Bucknell University
In Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering
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Approved by:

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I. Abstract

Atmospheric aerosol particles have been known to influence the Earth’s climate directly and indirectly. The magnitude of these effects strongly depends on their size, morphology, and their interaction with water at different relative humidities, yet our knowledge of them is largely limited. Moreover, many industrial processes such as food, personal care, and pharmaceuticals require a general knowledge of particles’ size and morphology. Therefore, an investigation of these characteristics is essential to both industrial and atmospheric applications. Different techniques have been used to study these physical characteristics of particles; nevertheless, these studies did not extend their analysis to the effects of different drying rates. Drying rates in this thesis are referring to different drying processes with different starting droplets and conditions. It was not the objective of this study to quantify the drying rates; therefore, the term was used to generally simplify the descriptions of two different drying processes. The thesis’ goal was to investigate the effect of drying rate on size and morphology of a few inorganic, amino acid and dicarboxylic acid (C3-C7) nanoparticles through the use of a scanning mobility particle spectrometer and an atomic force microscope. The hypothesis was that some chemical compounds resulted in different morphologies depending on the drying rates. Experimental results confirmed this hypothesis. Particularly, the even dicarboxylic acid particles (C4 and C6) did not change while the odd dicarboxylic acid particles (C3, C5 and C7) did. Both amino acids (glutamic acid and L-leucine) results showed that their
size stayed the same. However, AFM images of glutamic acid showed some changes in their morphology. Finally, CaCl₂ and NH₄Cl exhibited no change while NH₄NO₃ results indicated that the particles might have crystallized into two forms depending on the drying rates.
II. Introduction

Atmospheric aerosols are a collection of liquid or solid particles that are suspended in air. There are two sources of aerosols: natural sources and anthropogenic sources. Aerosols can be emitted naturally into the environment from volcanic eruptions, mineral dust, sea salt and biological materials (plant fragments, microorganisms, pollen, etc.) [Pöschl, 2005]. Additionally, human related sources such as biomass burning, incomplete combustion of fossil fuels, traffic-related suspension of road and other dusts account for about 10% of the total amount of aerosols in the atmosphere [Pöschl, 2005]. Their sizes range from less than 1 µm in radius which are called fine particles to 10 µm in radius which are coarse particles [Jacob, 1999]. Because of the difference in size and originated source, a region may contain a population of aerosols that is distinctive for that region. For example, coastal regions usually contain more salt aerosols than inland regions. On the other hand, the atmosphere above a big city may be more concentrated with traffic-related dusts than rural areas.

Atmospheric aerosols have been known to impose various effects on the atmosphere and the Earth’s climate, as well as human health. Studies show that aerosols directly and indirectly influence the Earth’s climate. By reflecting or absorbing incoming solar radiation, aerosol particles directly affect the Earth’s radiation balance [Seinfeld and Pandis, 1998]. Indirectly, aerosol particles can also act as cloud condensation nuclei which then turn into cloud droplets and alter the atmospheric conditions. In general,
atmospheric aerosols are believed to have a cooling or negative effect on the Earth’s climate [Liao et al., 2006; Hartmann and Doelling, 1991]. Additionally, cardiovascular, respiratory, and allergenic diseases are also thought to be caused by atmospheric aerosols [Pöschl, 2005]. The magnitude of these effects strongly depends on whether the particles are solid or aqueous [Martin, 2000; Martin et al., 2004] and how they interact with water, namely the hygroscopicity of particles.

The effects of atmospheric aerosols on the Earth’s climate and human health are so crucial, yet our understandings of their magnitude as well as what characteristics of aerosols dictate their influences, are still restricted (Figure 1). This uncertainty is largely due to our limited knowledge of how aerosols are formed and how they interact with water and/or other surrounding particles. Additionally, several physical properties such as size, structure and morphology essentially characterize the particles and their influences. Moreover, numerous studies revealed that a substantial concentration of sulfate and nitrate anions; ammonium and calcium cations; and low carbon-number dicarboxylic acids are presented in the atmosphere [Collett et al., 2002; Yang et al., 2004; Mader et al., 2004; Bilde and Svenningsson, 2004].

Therefore, this project is devoted to investigating size, morphology and how these properties change with respect to different drying processes. The study included both organic and inorganic aerosol particles, particularly CaCl₂, NH₄Cl, NH₄NO₃, glutamic acid, L-leucine, and C3-C7 dicarboxylic acids. The study utilized several innovative pieces of equipment such as a differential mobility analyzer (DMA), a condensation
particle counter (CPC) and an atomic force microscope (AFM) to extend our knowledge of atmospheric aerosols’ morphology in the nano scale.

**Figure 1.** Effects of atmospheric aerosols on climate and the level of scientific understanding of aerosols effects [IPCC, 2014].

It is important to note that the author used the term “drying rate” in the remaining parts of this thesis to simplify the descriptions of two different drying processes. Although there is not a simple way to quantify what the drying rates exactly are, it is obvious that they are different. The first drying process started with droplets that are dilute in concentration (1 g/L) and these droplets went through a series of diffusion dryers. The humidity system allowed the dried particles to be exposed to up to 89% RH conditions. Consequently, the second drying process started with much higher
concentration droplets (saturated solute concentrations) and they are smaller in size compared with the first process due to significantly less water. Therefore, the two processes must possess different drying rates.

To help guide the reader, this thesis is divided into eight sections: the previous abstract, the introduction, the background, the project scope, the materials and methods, the results and discussion, the conclusion and recommendations. The remainder of this document first focuses on the background information of the particles’ properties including size, morphology, and the hygroscopicity of particles. The project scope describes the thesis goals and discusses related previous studies. The next section is to give a description of what chemicals were investigated and experimental procedures that this study applied. The results and discussion section is divided into three sub-sections. The first one summarizes the results of calibration experiments that serve as a baseline for the rest of the data analysis. The second and third sub-sections describe the findings and proposed explanations for the hygroscopic behavior of dicarboxylic acids, amino acids and inorganic chemicals respectively. Finally, conclusions and recommendations for future work are drawn and described in the last section.
III. Background

This section gives a brief overview of some important characteristics of particles that were investigated in this project. The properties are size, morphology and hygroscopicity. In each of these characteristics, the description and motives of why they were studied in this project were explained.

1. Size

In the atmosphere, particles’ size plays a crucial part in determining how much solar radiation they can absorb or reflect and whether or not they can act as cloud condensation nuclei. Therefore, studying particles’ size will help predict mechanisms for which particles grow or crystallize in the atmosphere. One of the theories that describes the activities of atmospheric aerosols is the classic Köhler theory. The theory is based on the thermodynamic balance of the Raoult and Kelvin effects on the vapor pressure of water over a solution droplet. While this theory predicts that the chemical composition determines whether or not a particle is able to activate into a cloud droplet, recent studies have shown that cloud condensation nuclei (CCN) concentration can be accurately predicted without detailed knowledge of the chemical composition [Dusek et al. 2006; Ervens et al., 2007; Medina et al., 2007]. In fact, these studies showed that the particle size and the particle size distribution rather than chemical composition play a crucial role in determining its CCN activities in the atmosphere. Moreover, in terms of human health,
particles with different sizes impact at different places and have different effects on our respiratory system. For example, particles that are smaller than 10 μm in diameter have a greater threat to our health than larger particles because they can penetrate deeply into our lungs and, if small enough, even enter our blood streams [Rhodes, 2008]. Additionally, in many industrial processes such as food and pharmaceutical industries, particle size is also an important characteristic in various handling and processing operations.

There are several methods to measure and report particle size including sieving, microscopy, sedimentation, permeametry, electrozone sensing, and laser diffraction. Depending on the application, one or more of these methods can be chosen to quantify the particle size. For the purpose of this project, all particles were assumed to be spherical and their sizes were reported as their electrical mobility diameters unless otherwise noted. Atmospheric aerosols’ size can range from nanometers to over 100 microns. Particles that have size less than 1 μm in radius are categorized as fine particles and those that are bigger are considered coarse particles. This thesis primarily studied particles that were a tens to hundreds of nanometers in diameter. Moreover, this project used a scanning mobility particle spectrometer (SMPS) (described in the Materials and Methods section) to record and analyze particles’ size.
2. **Morphology**

Industrial processes require knowing not only the size and size distribution of particles, but also their morphology in order to have good controls over manufacturing and transporting solid particles. Particle morphology refers to particles’ shape, texture and the patterns of their surface [Tung et al. 2009]. For example, sphericle particles flow more freely than needle-like particles and mixing time for different shapes of particles varies greatly. Also, particle morphology is extremely important in the pharmaceutical industry because it determines how a drug is processed and delivered and what its effects inside a patient’s body are. In the atmosphere, particles also have various shapes and surface textures such as spherical, cubical, cylindrical or irregular shapes and even or uneven surfaces. Finally, it is important to understand particles morphology when we predict the particles’ ability to absorb or reflect the radiation from the sun. For example, non-spherical particles have a larger surface area than spherical particles.

Several pieces of equipment can be used to determine morphology of an individual particle or a group of particles. The most common tool is a scanning electron microscopy (SEM) which provides two dimensional images of a particle surface. The second most common technique is an atomic force microscope (AFM) which is more advanced than the SEM because it gives surface information in three dimensions. The SEM is best to analyze micron sized particles while the AFM is capable of imaging nanoparticles. Micron particles of a chemical compound might look different when they are reduced to the nanoscale. Moreover, even in the same scale, some chemical
compounds might possess different morphologies. Some morphologies of nanoparticles have been reported including nanotubes, nanowires, nano-whiskers, nano-rods, nano-belts, and nanofibers.
3. **Hygroscopicity**

As stated above, atmospheric aerosols affect the climate both directly and indirectly. Directly, atmospheric aerosols interact with the radiation from the sun and indirectly, they act as CCN which affects cloud properties. The magnitude of these effects, in fact, strongly depends on their interaction with water. Even when the relative humidity (RH) is less than 100%, aerosols can still take on water and grow into droplets. Hygroscopicity describes the ability of particles to absorb water at a given RH with a given initial dry diameter. Hygroscopic properties of aerosols depend on two factors: the ability of the solution droplet to lower the water activity, and their influence on surface tension (Ruehl et al., 2010).

A common technique that is used to measure the hygroscopicity of a specific compound is hygroscopic tandem differential mobility analyzer (HTDMA). Through this technique, a hygroscopic growth factor (GF) is measured along with the changes in particles size and phases. The GF can be expressed as:

\[
GF = \frac{D_p(RH)}{d_s(RH)}
\]  

In the above equation, \(D_p(RH)\) is the wet particle diameter at a given higher RH compared to \(d_s(RH)\) which is the dry particle diameter at a set lower RH so that when GF=1 there is no water uptake. At a phase transition RH, called the deliquescence RH (DRH), the solid particle abruptly deliquesces and forms a saturated solution droplet (Gysel et al., 2002). In other words, the particles remain the same phase until this DRH is
reached. Recent studies show that hygroscopic properties are particle size dependent (Biskos et al., 2006; Park et al., 2009; Russell et al., 2002) and ambient RH dependent (Hu et al., 2010). For example, when RH is below the DRH, GFs of NaCl aerosols decrease while dry particle diameter increases (Hu et al., 2010). When RH reaches the DRH, GFs increase with dry particle diameter (Hu et al., 2010). Large particles are easier to uptake water than smaller particles, but only when there is enough water vapor. Hu et al. (2010) also concluded that there were two regimes of effects: RH dominant regime (below DRH) where GFs increased with RH and particle size dominant (above DRH) where GFs were more sensitive to particle size.

While there are many studies on the hygroscopicity of inorganic aerosols, there is very limited information on the water interaction of organic aerosols. Posfai et al. (1998) concluded that organic aerosols were responsible for water uptake of ammonium sulfate at low RH. Another study included that film coatings of several organic species delayed the hygroscopic growth of sulfuric acid aerosol in the first few seconds (Xiong et al., 1998). These two results contradict each other, so more studies are needed to understand the hygroscopic growth of organic aerosols.
IV. Project Scope

The following section outlines the main goals of this project. The second half of the section reviews previous studies of size, morphology and hygroscopicity of particles using different techniques.

1. Research Goals

As seen in the introduction, atmospheric particles’ properties play a crucial part in the variation of the Earth’s climate. Particularly, their size and morphology determine how much reflection or absorption of solar radiation they could have. Moreover, aerosols can act as cloud condensation nuclei which in turn become cloud droplets. Once formed, clouds can have a tremendous effect on the Earth’s radiation budget through their albedo [IPCC, 1995]. So, either directly or indirectly, atmospheric aerosols have a tremendous impact on our environment and our daily life. Additionally, when particles travel through a different ambient RH, they can take up water and grow bigger or they can shrink and crystallize. Therefore, investigating particles’ size and morphology after they are undergone different drying processes will help propose mechanisms for which particles grow or crystallize and how they behave in the atmosphere. Furthermore, the understanding of water-particles interaction will help predict the effects of aerosol particles on the global climate.
In addition, nanoparticle science is currently a growing topic because of its various properties and applications. Bulk materials might have different properties when their sizes are reduced to the nanoscale. Those unique properties are sometimes desirable and sometimes not, depending on the application. Therefore, many industrial processes are interested in investigating nanoparticles’ properties in order to have better control in their synthesis and production. For example, in the pharmaceutical industry, different polymorphs of an active ingredient might have varied solubility which affects the drug’s bioavailability and efficiency. Different morphologies of nanoparticles have been reported including nanotubes, nanowires, nano-whiskers, nano-rods, nano-belts, and nanofibers [Wei-Ning et al., 2005; Ali and Ali, 2011]. Therefore, expanding our study of particles’ properties to the nanoscale has potential benefits in both industrial and atmospheric applications.

As summarized in the Literature Review section, nanoparticles’ properties and their interaction with water above the DRH condition are well understood; however, prediction of whether or not their properties change once the particles are re-dried is not fully developed. Furthermore, atmospheric researchers have generated particles using different techniques, dried them and then analyzed them assuming that they are perfectly spherical and have the same size [Pitchumani et al., 2006; Lind et al., 2010; and Akgün et al., 2013]. Those data are then used to extrapolate to what really happens in the atmosphere. However, in reality, particles are produced, subjected to different RHs and may undergo morphological re-conformations. These particles might or might not have a spherical shape. For example, atmospheric researchers generate salt particles in their
laboratories and extrapolate their results to what really happens in the coastal atmosphere. This study desired to show that particles from a pure chemical could form different mobility sizes and shapes depending on the drying cycles that they went through, and that results from our lab generation methods do not necessarily represent real events in the atmosphere. Particularly, this thesis’ goals are:

1. to investigate the size and morphology of selected inorganic and organic particles after they went through a series of diffusion dryers (less than 10% RH) and

2. to compare those properties to those that were humidified and then dried again in the second drying process (<10% RH $\rightarrow$ >85% RH $\rightarrow$ <10% RH).

A full list of inorganics and organics that were investigated in this thesis and their manufactures can be found in the following Materials and Methods section.

Experiments involved constructing an apparatus that allows and directs particles to travel through different settings of RH. The work also made use of several other techniques including an aerosol atomizer to generate aerosols, diffusion dryers, a PIXE impactor and mica discs to collect particles of different sizes, a differential mobility analyzer (DMA) and a condensation particle counter (CPC) to analyze particles’ mobility diameters and compute the size distribution. Furthermore, this thesis featured the most innovative imaging technique via atomic force microscopy which allows a three dimensional morphology investigation of nanoparticles.
2. Literature Review

This section reviews a few studies that investigated the interaction of selected nanoparticles with water. Each study had its own unique approaches which were used as a framework for this project. In addition, each study also had their advancements and limitations. Some studies were able to achieve high RH conditions but did not have the appropriate optical analysis to show the changes in particles’ morphology. Some other studies incorporated optical analysis but were not able to get to high RH. Moreover, there is not a study examining if aerosol properties change when they are experience more than one cycle of drying. This project attempted to address some of these limitations.

a) Characterization of Particles

Various approaches exist for identifying and characterizing nanoparticles; however, they mostly fall under two categories: aerodynamic mobility sizing and direct imaging microscopy. Mobility sizing typically includes a condensation particle counter combined with a differential mobility analyzer. Imaging microscopy includes the scanning electron microscope (SEM), environmental scanning electron microscope (ESEM), transmission electron microscope (TEM) and atomic force microscope (AFM). Each technique has its own advantages and disadvantages. For example, in order to be analyzed under the SEM, samples need to be conducting and are subjected to a vacuum environment. Although the SEM operates faster than the AFM and gives the user real
time interaction, samples can be damaged from the high energy of the electron beam. The AFM doesn’t require a vacuum mode or conducting samples, but it is limited to a few microns in height (z-range) and requires a very flat substrate for collection and imaging. More information about the techniques that were used in this study is available in the next section.

Most studies about the interaction of particles with water use the SEM, ESEM or the TEM technique. One example of those studies is the study of sodium nitrate particles by R. C. Hoffmann et al. [2004]. The paper reported that NaNO₃ particles in a form of amorphous solid were ready to take up water even at low RH. NaNO₃ particles were exposed to 85% RH and then dried under vacuum in the SEM chamber. Resulting images showed that the particles did not re-form a crystalline structure. However, the authors also recognized that the particles’ properties might already be damaged by the electron beam of the SEM.

Another study investigates the hygroscopic property, chemical composition and morphology of NaCl aerosol particles by combining optical and electron microscopy techniques [Ahn et al., 2010]. They utilized 2D images from the SEM and a quantitative energy-dispersive electron probe X-ray microanalysis, named low-Z particle EPMA, to analyze particles’ properties at different RH conditions. Their results for NaCl showed that at low RH (2.4% to 74.5%), NaCl particles have a rectangular shape and when RH increased up to 75.3%, all particles absorbed water and looked circular. As the RH continued increasing, the NaCl particles rapidly absorbed more water and dissolved completely at 75.7% RH. The NaCl droplets grew bigger in size up to 94% RH. The
opposite process which is the dehydration process showed similar results. As the RH dropped from high to low, the NaCl droplets started shrinking and recrystallized at 47.7% RH. A similar approach was applied for KCl, (NH₄)₂SO₄ and Na₂SO₄ particles and the results are comparable. One limiting factor in this study is that they interpret the growth factor of particles based on 2D images which resulted in a large uncertainty in estimating particles’ volume.

The third study focused on the hygroscopic growth of (NH₄)₂SO₄ particles at a high RH between 90% and 98% [Hennig et al., 2005]. They designed a high humidity tandem differential mobility analyzer (HHTDMA) which is similar to this study’s apparatus with an additional differential mobility analyzer (DMA) that is connected to a temperature control. They also utilized Nafion membrane tubes that this study also includes in our humidity control system (described in the next section). The results showed that an increase in RH yields an increase in particle diameter. Although this study was able to investigate particle size at high RH (up to 98%), they did not incorporate any optical techniques to see the difference in morphology when the particles were exposed to different RHs.

Another study that is important to mention is an investigation of hygroscopic growth of multicomponent aerosol particles subjected to several cycles of RH [Rosenoern, 2007]. The study used an infrared aerosol flow tube and cycled RH between 3% and 66%. The investigating mixtures were ammonium, sulfate and hydrogen ions. By reading the infrared spectrum, they determined the particle’s phase (droplet or crystal). The study results showed that the physical state and hygroscopic growth of aerosols
could be affected by multiple cycles of RH. Furthermore, cycling between low and medium RH might have a larger effect on particles’ properties than high RH. Although the results of this study are significant, like Hennig et al. [2005], they did not include any optical analysis.
b) Drying cycle

Although there are various studies investigating the hygroscopicity of particles at high RH and how particles’ properties change during the humidification process [Hu et al., 2010, Cruz and Pandis, 2000, Ruehl et al., 2010, Ebert et al., 2002, and Hennig et al., 2005], there are none examining what happens if particles go through the drying process again. Previous studies indicated that within the deliquescence RH (DRH) threshold, NaCl and PbS particles experienced a microstructural rearrangement which might cause a size reduction up to ~50% [Krämer et al., 2000 and Mikhailov et al., 1997]. Furthermore, TEM images in a recent study showed that the initial cubic shape of dry salt particles transformed to near-spherical shape at RH > DRH [Shi et al., 2012]. The same study also confirmed that benzoic acid particles underwent a microstructure rearrangement during the humidification process which caused a near-spherical shape at low RH to change to a cylindrical shape at 80% RH. Similar results with NaCl were also found with Na₂SO₄, (NH₄)₂SO₄ and NH₄NO₃ [Ebert et al., 2002]. All of these studies clearly indicated that there was a change in morphology when particles were exposed to high RH, so the next phase is to investigate the change in morphology of particles when they are dried for a second time. Furthermore, one study showed that NaCl particles when dried slowly (5.5 ± 0.9 RH/s) experienced slower evaporation and crystallization, which led to sharper edges (or cubic shape) and when dried quickly (101 ± 3 RH/s), the evaporation and crystallization were more rapid, which caused softer edges (or spherical shape) [Wang et
al., 2010]. Therefore, the rate of drying also plays an important factor in shaping the morphology of particles.
V. Materials and Methods

This section gives an overview of what materials were investigated in this study as well as a description of the apparatus that was set up to modify the humidity condition of the aerosol stream. The last segment of this section describes the analytical instrument that was utilized to examine the particles’ size and morphology.

1. Materials and Sampling Discs

All initial solutions in this study had a concentration of 1.0 g/L using double deionized ultrafiltered water to ensure minimal impurities. The solutes were either inorganic or organic compounds. Inorganic chemicals that were investigated in this study were CaCl₂, (NH₄)₂SO₄, NH₄NO₃, and NH₄Cl (Table 1). Organic compounds were glutamic acid, leucine, adipic acid, glutaric acid, succinic acid, pimelic acid and malonic acid (Table 1). Those chemicals were chosen because they are either abundant in the atmosphere or are popularly used in the pharmaceutical industry. Each solution was stored in a 60 mL syringe with a syringe needle. This syringe was inserted into a collision atomizer which produced polydisperse particles (described in more details in the following section).

Particles were collected on a 12 mm steel disc that had a carbon tape covering the top. Each sample disc also had a mica disc attached on top of the carbon tape in order to
view under an atomic force microscope (AFM). Mica is a silicate mineral that provides a perfectly clean and flat surface on which to impact the nanoparticles for imaging.

**Table 1. List of Studied Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Formula</th>
<th>Type</th>
<th>Supplier</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonic Acid</td>
<td>HOOC-CH₂-COOH</td>
<td>Dicarboxylic acid</td>
<td>Alfa Aesar</td>
<td>99</td>
</tr>
<tr>
<td>Succinic Acid</td>
<td>HOOC-(CH₂)₂-COOH</td>
<td>Dicarboxylic acid</td>
<td>Alfa Aesar</td>
<td>99</td>
</tr>
<tr>
<td>Glutaric Acid</td>
<td>HOOC-(CH₂)₃-COOH</td>
<td>Dicarboxylic acid</td>
<td>Alfa Aesar</td>
<td>99</td>
</tr>
<tr>
<td>Adipic Acid</td>
<td>HOOC-(CH₂)₄-COOH</td>
<td>Dicarboxylic acid</td>
<td>Alfa Aesar</td>
<td>99</td>
</tr>
<tr>
<td>Pimelic Acid</td>
<td>HOOC-(CH₂)₅-COOH</td>
<td>Dicarboxylic acid</td>
<td>Acros Organics</td>
<td>98</td>
</tr>
<tr>
<td>L - Glutamic Acid</td>
<td><a href="COOH">CHNH₂(CH₂)₂</a>₂</td>
<td>Amino acid</td>
<td>Acros Organics</td>
<td>99</td>
</tr>
<tr>
<td>L - Leucine</td>
<td>(CH₃)₂CHCH₂CH(NH₂)COOH</td>
<td>Amino acid</td>
<td>Acros Organics</td>
<td>99</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>CaCl₂</td>
<td>Inorganic</td>
<td>FisherBiotech</td>
<td>99</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>NH₄Cl</td>
<td>Inorganic</td>
<td>Acros Organics</td>
<td>99</td>
</tr>
<tr>
<td>Ammonium Nitrate</td>
<td>NH₄NO₃</td>
<td>Inorganic</td>
<td>Acros Organics</td>
<td>99</td>
</tr>
</tbody>
</table>
2. Apparatus Set-up

The experimental setup is shown in Figure 2. The apparatus consisted of 5 main sections: the Monodisperse Aerosol Generation system, the Size Selecting system, the Humidity Control system, the Scanning Mobility Particle Sizing system (SMPS), and the particles collecting system. The main parts of the Monodisperse Aerosol Generation system includes an aerosol atomizer (Constant Output Atomizer 3076, Thermo Systems Inc. (TSI)) and diffusion dryers. The Size Selecting system has a neutralizer (Aerosol Neutralizer 3077, TSI), and a differential mobility analyzer (DMA 1) (3080, TSI). The Humidity Control system includes a copper pipe with low RH (dry line), 2 sets of Nafion tubes, a water bath to humidify particles (wet line), a diffusion dryer and a temperature and RH meter (Vaisala HMT 330) to record the final condition of the particles. The SMPS system includes a second set of neutralizer and DMA 2 (3080, TSI) and a condensation particle counters (CPC) (3775, TSI). A PIXE impactor and a vacuum are set up at the end of the apparatus to collect particles. The setup allows the operator to have control over the particles’ size and the humidity of particles simultaneously. More details of these systems are described in the following sub-sections.

1 The experimental procedure and set-up to the DMA was precisely the same as that of the author’s undergraduate Honor Thesis study. Therefore, the author took the liberty to adopt the corresponding Experimental sections in her Honor Thesis in this proposal.
Figure 2. A schematic of the experimental setup
**a) Monodisperse Aerosol Generation System and Size Selecting System**

The study used a collision atomizer that produces polydisperse drops of the investigated species. The atomizer uses a high velocity air jet to provide a constant output. Filtered air is introduced into the stream to generate droplets. Then, the solution stream enters a series of five silica gel diffusion dryers to evaporate the solvent. At this stage, the particles exit with a smaller size and are dry. This wide size distribution of polydisperse particles is then charged in a Kr-86 bipolar aerosol neutralizer. In this neutralizer, the particles achieve a nearly Boltzmann equilibrium distribution of charges [Wiedensohler, 1988]. From the neutralizer, the particles continue to travel into the DMA 1. By adjusting the voltage of the center rod in the DMA, desired diameters are selected according to their electrical mobility [Liu and Pui, 1974; Knutson and Whitby, 1975]. The particles exiting the DMA 1 have similar size with each other (± 2nm [tsi.com]). The operator can arrange the experimental setup to have the particles stream skip the neutralizer and the DMA 1. This alternative setup will allow all the particles with different sizes to enter the reaction chamber through the dry line or the wet line. The selection of size will take place inside the PIXE impactor at the end of the setup instead (more details in the PIXE section).

Each diffusion dryer is a concentric tube. The outer tubes are filled with silica gel and the particles stream pass through the inner tube (Figure 3). Silica gel or silicon dioxide pellets absorb moisture from the particles stream and fill their interconnected pores. The dryers need to be recharged once the pellets become fully saturated. The
preliminary study showed that the particles stream exiting the diffusion dryers was at approximately 5% RH. The silica gel is washed with cobalt chloride and has a blue color when it is dry and turns pink when it becomes saturated. At that point, the silica gel is put in an oven at 90°C for 3.5 hours to evaporate all water contents and let cool for 2 hours before being put back into the dryers.

**Figure 3.** Diagram of a diffusion dryer (Laura Cook Thesis Proposal)
b) Humidity Control System

The particles stream exiting the diffusion dryers or the DMA 1 is directed into either the dry line (RH < 10%) or the wet line (RH > 85%). Control valves are set at each end of these lines to allow the operator to have control over which line the stream will flow through before entering the reaction chamber. The reaction chamber consists of a temperature probe and a RH probe that are connected to a Vaisala meter. Temperature and RH data can be recorded to a computer at an increment of one reading per second. The dry line is a copper tube that permits all dry particles from the previous unit to go through without altering their RH condition. The wet line consists of 2 (48 inches) Nafion membrane tubes (Perma Pure) that are connected to a water bath externally. Dry stream passes through the inside tube of the Nafion tubes and the distilled water cycles between the outer tube of the Nafion and the water bath. The Nafion membrane is a semi-permeable membrane that allows water to diffuse into the dry stream and increase its RH up to 89%. After the Vaisala meter indicates an RH above 85%, an additional diffusion dryer is connected at the end of the wet line to bring the RH back to below 10%.
c) **Scanning Mobility Particle Sizing System**

The particles stream exits the reaction chamber and enters the second neutralizer and the DMA 2. This second set of neutralizer and DMA do the exact same task as the first ones (described in the Monodisperse Aerosol Generation System and Size Selecting System section). The only difference is that the second DMA is set to sample all particles with different sizes. The particles continue to travel to the CPC where they are detected and counted continuously by a laser. The CPC 3775 can detect particles down to 4nm and measure their concentration up to $10^7$ particles/cm³ [http://www.tsi.com/Condensation-Particle-Counter-3775/]. Moreover, it is connected to a computer to display the particles’ size distribution simultaneously. The AIM software in the computer manages the data that are sent from the CPC every 0.1 seconds during each scan.
d) PIXE Impactor

A PIXE impactor is used to collect particles at the end of the apparatus setup. The impactor uses inertial impaction to collect aerodynamically fractionated particulate samples [www.pixentr.com]. The impactor consists of 9 stages (Figure 4) that only allow specific diameters to pass through. The size ranges from < 0.06μm to >16μm. As seen in the following figure, the upper stages will impact larger particles and the bottom stages will only allow small particles to pass through. The sample discs that were described in the Materials and Sampling Discs section are attached to the bottom of each stage. The mica sample discs are attached to stage L1, L2, 1 and 2 to collect particles with a variety of sizes to view under the AFM. Those stages are only connected for a few minutes after the system reaches steady state to prevent too many particles from impacting on the sample plates.
Figure 4. Cutaway View of the PIXE Impactor
3. **Analytical Instrument**

Size distribution of particles is analyzed using the TSI Aerosol Instrument Manager (AIM) software while the morphology of those collected particles are viewed and analyzed using an atomic force microscope (AFM). This section gives a brief description of the AFM instrument.

To obtain three dimensional images of nanoparticles, an atomic force microscope (AFM) (Veeco Multimode V) is utilized in this study. The instrument consists of a cantilever that has a thin and sharp tip that can move up and down to scan a surface (Figure 5) and a laser light that shines at an angle down to the cantilever and reflects back on to a quadric photodiode. Each section of the photodiode can generate a corresponding voltage and sends those signals to a computer. By tracking the motion of the cantilever, an accurate three dimensional image of the surface can be depicted. AFM can be used for various applications such as imaging, measuring surface properties (force, compliance, cohesion) or manipulating objects on a surface. There are two operating modes that one can choose on the AFM: a contact mode where the tip actually touches the sample and a tapping mode where the tip only taps across the surface. The contact mode can have high pressure and cause damage to the surface, displacements of weakly bound adsorbates or disturbance of viscous surfaces. Because the tip essentially touches the sample surface, it can contaminate the tip or the sample if the study investigates more than one type of chemical. In this study, samples were analyzed using the tapping mode. Although the AFM does not require a vacuum mode and a conducting surface like the SEM, there is a
limit in the z-range which is not more than a few microns. The sample size is also limited compared with the SEM and the operator can only interact with a small region of the sample surface at a time.

![Diagram of Atomic Force Microscope](image)

**Figure 5.** Diagram of Atomic Force Microscope [Veeco]
VI.  Results and Discussion

This section is divided into three sub-sections. The first sub-section is to explain and lay out the baseline for data analysis that was applied in this thesis. The second sub-section discusses the results found in the dicarboxylic acid experiments. The last sub-section reviews the results found in experiments with amino acids and inorganic compounds.

1.  Calibration of the experimental set-up

The apparatus was set up to measure temperature and RH over time as well as to humidify an aerosol stream to above 85% RH. This set-up was validated in the preliminary experiments (Appendix A). In addition, three sets of experiments were conducted to ensure that the scanning mobility particle spectrometer (SMPS) operated properly. The additional experiments were also to investigate how many particles were lost between the dry setting and the dry-wet-dry (DWD) setting. This shortfall of particles was due to the additional tubes and connectors in the DWD setting.

The first two sets of experiments inspected NIST particles nominally sized 80 nm and 200 nm. Those polymer particles were manufactured to have perfectly uniform spherical shapes with very narrow size distributions. They were also not soluble in water so their sizes would not alter regardless of the drying process. These two sizes were
chosen because the majority of particles that were investigated in this study were between 80 nm and 200 nm.

Figure 5 shows the comparison of two size distributions of the 80 nm NIST particles that were measured using the scanning mobility particle spectrometer (SMPS) in dry and DWD conditions. The blue line which represents the size distribution of the polymer particles in dry condition has a mode (averaged mode from all scans) of 82.0 nm. Total concentration has an average of approximately 6000 particles/cm³. The red line represents the size distribution of the polymer particles that were humidified to above 85% RH then re-dried to less than 10% RH (DWD setting). The mode (averaged from all scans) of this distribution is 82.8 nm. Total concentration has an average of approximately 4,400 particles/cm³. As a result, the DWD setting with additional tubes lost about 27% total concentration compared with the dry setting, but the aerosols’ sizes remained the same, as expected.
Figure 5. Size distribution of 80 nm NIST nanospheres measured in dry condition (<10% RH) (blue line). The nanospheres were humidified to >85% RH then re-dried to <10% RH (DWD condition). Their distribution was measured again (red line). The modes of both distributions (averaged from all scans) are 82.0 nm and 82.8 nm respectively.
Similarly, Figure 6 shows the comparison of two size distributions of the 200 nm NIST particles that were measured using the SMPS in dry and DWD conditions. The blue and red lines represent the size distributions of the polymer particles in dry condition and in DWD condition respectively. The mode (averaged from all scans) of both distributions is 187.7 nm. Total concentrations of the dry and DWD conditions are 764 particles/cm³ and 442 particles/cm³ respectively. As a result, the DWD setting lost about 42% total concentration compared with the dry setting, but the particles’ sizes remained the same, as expected.

These two sets of experiments provided a few conclusions. First, the SMPS measured aerosols’ size distributions accurately to the degree of ±3 nm. Secondly, the polymer nanospheres’ size remained the same before and after the humidification process as expected. Thirdly, the particles’ total concentration of the DWD condition was less than that of the dry condition in both sizes due to the wall loss from the additional tubes (ranging from 27% to 42%). Fourthly, 80 nm particles tend to stick to the walls of the tubes less than 200 nm particles.
Figure 6. Size distribution of 200 nm NIST nanospheres measured in dry condition (<10% RH) (blue line) and DWD condition (> 85% then <10% RH) (red line). The modes of both distributions (averaged from all scans) are 187.7 nm.
The third set of experiments investigated ammonium sulfate particles in dry and DWD conditions using the same procedure as the polymer spheres. Ammonium sulfate has been widely studied and used as a calibration substance. Ammonium sulfate morphology is reported to be spherical and remains spherical with different RH’s [Wise et al., 2005 and Cook, 2011]. Therefore, in both dry and DWD conditions, ammonium sulfate particles’ size distribution should remain unchanged. A normalized size distribution was constructed (each number of concentration was divided by the maximum concentration) to better show the overlap between the dry and DWD size distributions accounting for losses in the DWD runs. The original size distributions which display the loss of total particles concentration between the dry and DWD conditions due to additional tubes are shown in Appendix B. As seen in Figure 7, the size distribution mode increases from 81.9 nm in dry condition to 94.4 nm in DWD condition. Some of the particles might not dry completely and as a result, the size distribution is shifted to the right slightly. This shift in the size distribution was used as a reference calibration for other compounds’ size distributions. In other words, a difference of 15 nm or less may be considered unchanged in morphology.
Figure 7. Normalized size distribution of ammonium sulfate particles measured in dry condition (<10% RH) (blue line) and in DWD condition (> 85% then <10% RH) (red line). The modes of both distributions (averaged from all scans) are 81.9 nm and 94.4 nm respectively.
2. Dicarboxylic Acids

The first set of organic chemicals that was studied in this thesis was dicarboxylic acids (C3-C7). Some physical properties of these acids are listed in Table 2. Particle size and morphology is determined by many factors including their melting points, boiling points, densities, solubility in water and vapor pressures. Pankow [1994] pointed out that vapor pressure was an important parameter to model partitioning of low volatility organic compounds between gas phase and particle phase; therefore, it was included in the physical properties table. For the remainder of this paper, dicarboxylic acids will be referred to as “odd” or “even”, which refer to the number of carbon atoms in the acid chain.
### Table 2. Physical properties of investigated dicarboxylic acids at 25°C<sup>a</sup>

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>MW g/mol</th>
<th>Melting Point, °C</th>
<th>Boiling Point At 13.3kPa, °C</th>
<th>Density 25°C, g/cm³</th>
<th>Solubility in H₂O, g/L, 25°C</th>
<th>&lt;sup&gt;b&lt;/sup&gt;Vapor Pressure, 25°C, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonic Acid</td>
<td>HOOC-CH₂-COOH</td>
<td>104.06</td>
<td>135</td>
<td>-</td>
<td>1.619</td>
<td>1668.1</td>
<td>3.6 x 10⁻⁴</td>
</tr>
<tr>
<td>Succinic Acid</td>
<td>HOOC-(CH₂)₂-COOH</td>
<td>118.08</td>
<td>188</td>
<td>235</td>
<td>1.572</td>
<td>88.3</td>
<td>3.9 x 10⁻⁵</td>
</tr>
<tr>
<td>Glutaric Acid</td>
<td>HOOC-(CH₂)₃-COOH</td>
<td>132.11</td>
<td>99</td>
<td>200</td>
<td>1.424</td>
<td>1118.7</td>
<td>6.7 x 10⁻⁴</td>
</tr>
<tr>
<td>Adipic Acid</td>
<td>HOOC-(CH₂)₄-COOH</td>
<td>146.14</td>
<td>153</td>
<td>265</td>
<td>1.360</td>
<td>25.0</td>
<td>9.8 x 10⁻⁶</td>
</tr>
<tr>
<td>Pimelic Acid</td>
<td>HOOC-(CH₂)₅-COOH</td>
<td>160.17</td>
<td>106</td>
<td>272</td>
<td>1.329</td>
<td>67.7</td>
<td>5.1 x 10⁻⁵</td>
</tr>
</tbody>
</table>

<sup>a</sup> Clark, 1986.

<sup>b</sup> Bilde et. al., 2003.
Size distributions of C3-C7 dicarboxylic acids were measured and analyzed for both the dry and DWD conditions. For each set of data that exhibited a change in size, DMA 1 was used to pre-select a size before the particles entered the humidification line. Their size distributions were measured again using DMA 2 to confirm the change that was observed in the initial size distributions. In these cases, the particles were also collected in the PIXE and imaged in the AFM. The results showed that the even acids exhibited no change in their size while the odd acids did.

\textbf{a) Even acids – morphology unchanged}

A normalized size distribution was constructed for C4 and C6 dicarboxylic acids to better show the overlap between the dry and DWD size distributions (Figure 8). The original size distributions which display the loss of total particles concentration between the dry and DWD conditions due to additional tubes are shown in Appendix B. The dry distribution of succinic acid has a mode (averaged from all scans) of 94.8 nm which is larger than what Cook (2011) reported (64 nm). However, Cook’s study used a higher pressure (35 psi) in the atomizer than this thesis (30 psi) and she was able to achieve a lower RH than this thesis. On the other hand, this work produced smaller sizes compared to the results from Bilde et al. (2003) (151 nm). Their experiments were at higher temperature than this study. The mode (averaged from all scans) of the DWD condition (90.5 nm) is in close agreement with that of the dry condition. In addition, AFM images
of particles collected from the dry and DWD conditions also confirm the result and are included in Appendix C. Note that AFM images show spherical particles, as expected.

Figure 8. Normalized size distributions of succinic acid particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 94.8 nm and 90.5 nm respectively.
Similarly to succinic acid, normalized size distributions of adipic acid are shown in Figure 9. Although the two distributions are not in as good agreement as in the succinic acid case, their sizes are still considered unchanged according to the ammonium sulfate calibration. Moreover, the dry distribution mode (averaged from all scans) is in good agreement with Cook’s study (2011) (95 nm and 103.6 nm). In addition, AFM images of particles collected from the dry and DWD conditions also confirm the result and are included in Appendix C. Note that AFM images show cylindrical plate-like particles.
Figure 9. Normalized size distributions of adipic acid particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 103.7 nm and 115.7 nm respectively.
b) **Odd acids – morphology change**

The properties of odd dicarboxylic acids have been extensively studied in the past. The earliest recognition of their unusual behavior compared with the even acids was Baeyer’s work in 1877. His work reported the alternation in melting point in dicarboxylic acids. The odd acids have lower melting point than the even ones. After his work, other studies investigated further and reported the same phenomenon in other physical properties for solids. Odd acids’ particles morphologies were also widely studied with different techniques such as X-ray and optical microscopes. Thalladi et al. [2000] summarized these studies, which all agreed that the odd acids exhibit different properties with the even ones. This study looked at these dry, odd dicarboxylic acid particles and extended the investigation to DWD particles.

i. **Malonic Acid – C3**

Size distributions of malonic acid in dry and DWD conditions are shown in Figure 10. As seen in the figure, the DWD distribution is contained within the Dry distribution which indicated that particles did not grow bigger in the second drying process. However, the smaller particles were significantly lost in the process which explains why the mode (averaged from all scans) of the DWD distribution became larger. As shown in Table 2, the vapor pressure of malonic acid is sufficiently high ($3.6 \times 10^{-4}$ Pa) that the smaller particles may have evaporated before they entered the second DMA.
This hypothesis was confirmed when the DMA 1 was used to pre-select a size and re-measure their distributions in the DMA 2. Figure 11 and 12 show size distributions of pre-selected 50 nm and 100 nm dry particles after they went through the humidification and re-drying process. Both sets of data concluded that there was no change in their distributions (modes that were averaged from all scans remained 50 and 100 nm). However, there was practically no particle measured in the DMA 2 for the 20 nm pre-selected dry particles. This result indicates that malonic acid might have formed two types of particles in the slow drying process and the newly formed particles had a smaller dimension that was detected by the DMA.
Figure 10. Size distribution of malonic acid particles measured in dry condition (<10% RH) (blue line) and in DWD condition (> 85% then <10% RH) (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 52.2 nm and 80.7 nm respectively.
Figure 11. Size distribution of malonic acid particles measured in DWD condition. The particles’ size was pre-selected using the DMA1 to be 50nm before entering the humidification process. The mode (averaged from all scans) is 47.5 nm.
Figure 12. Size distribution of malonic acid particles measured in DWD condition. The particles’ size was pre-selected using the DMA1 to be 100 nm before entering the humidification process. The mode (averaged from all scans) is 90.4 nm.

The two-morphology hypothesis was also confirmed by the AFM images. As shown in Figure 13, the dry particles exhibit a round or spherical shape. But in Figure 14, the DWD particles have sharper edges and are more like thin plates. In other words, when malonic acid particles were dried in the first time, they formed spherical particles and when they were dried slowly in the second time, they formed plate-like particles.
Figure 13. AFM image and profile graphs of selected Malonic Acid particles in Dry condition (<10% RH). The image and profile graph show mostly spherical particles.
Figure 14. AFM image and profile graphs of selected Malonic Acid particles in DWD condition (<10% RH, >85% RH, <10% RH). The image and the profile graphs show mostly plate-shape particles.
**ii. Glutaric Acid – C5**

Glutaric acid size distributions of dry and DWD conditions are shown in Figure 15. As seen in the figure, the dry aerosols’ distribution has 2 modes. One mode is approximately 30 nm and the second is around 110 nm. On the other hand, the DWD particles’ distribution only has one mode around 40 nm. It is possible that the high vapor pressure of glutaric acid is responsible for this unusual distribution or that the initial drying process of the dilute atomized solution results in two distinct particle morphologies with different mobility diameters (as measured with the SMPS).
Figure 15. Normalized size distributions of glutaric acid particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The mode (averaged from all scans) of the DWD distribution is 37.5 nm. The dry distribution has 2 modes at approximately 28 nm and 110 nm.

Similarly to malonic acid, the DMA 1 was used to pre-select a size to verify the change in size distribution. Figure 16 and 17 show size distributions of the pre-selected 28 nm and 110 nm dry particles after the alteration respectively. The dry particles were
sent through the humidification and re-drying process before they were measured again in the DMA 2. As shown, both distributions have modes around 50 nm. This confirms the results shown in the overall distributions, indicating that both the 28 nm and 110 nm mobility diameter particles were transformed by humidification cycling into the same 50 nm mobility size.

**Figure 16.** Size distribution of glutaric acid particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 28 nm before entering the humidification process. The mode (averaged from all scans) is 53.0 nm.
Figure 17. Size distribution of glutaric acid particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 110 nm before entering the humidification process. The mode (averaged from all scans) is 48.5 nm.

Pre-selected dry particles were also collected by the PIXE impactor and analyzed under the AFM. The images and profile graphs of 28 nm and 110 nm dry particles are shown in Figure 18 and 19 respectively. The AFM image of the 28 nm dry particles shows mostly spherical particles while the 110 nm image shows a mixture of rounded-shape and sharp-edge particles. The DWD particles were also collected and analyzed under the AFM. As shown in Figure 20, the particles have sharp edges similar to some particles from the 110 nm image. In other words, glutaric acid particles crystallize to different forms when they are dried at different rates. In the fast drying rate from a dilute
concentration, glutaric acid formed two different morphologies. As a result, the glutaric acid SMPS distributions appeared to have two modes due to the different mobilities of the two shape profiles. In the slow drying rate from a concentrated solution, glutaric acid particles appeared to re-arrange their structures and formed only one morphology which demonstrated by the single 40-50 nm mode normal distribution.
**Figure 18.** AFM image and profile graphs of dry glutaric acid particles. The particles’ size was pre-selected in the DMA 1 to be 28 nm before collected in the PIXE. Mostly spherical particles are shown.
Figure 19. AFM image and profile graphs of dry glutaric acid particles. The particles’ size was pre-selected in the DMA 1 to be 110 nm before collected in the PIXE. Both round shape and sharp edge particles are shown.
Figure 20. AFM image and profile graphs of selected Glutaric Acid particles in DWD condition (<10% RH then >85% RH then <10% RH). The image and the profile graphs show some sharp edge particles.
iii. **Pimelic Acid – C7**

Size distributions of pimelic acid in dry and DWD conditions are shown in Figure 21. As seen in the figure, the DWD distribution is contained within the dry distribution, which indicated that the particles did not grow bigger in the second drying process. However, the smaller particles were significantly lost in the process which explains why the mode (averaged from all scans) of the DWD distribution became slightly larger. As shown in Table 2, the vapor pressure of pimelic acid is high but is not as high as that of malonic acid and glutaric acid.
Figure 21. Size distribution of pimelic acid particles measured in dry condition (<10% RH) (blue line) and DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 129.5 nm and 148.2 nm respectively.

The DMA 1 was used to verify the change in size distribution. It was utilized to pre-select a size and re-measure the distribution in the DMA 2. Figure 22 and 23 show size distributions of pre-selected 130 nm and 210 nm dry particles after they went through the humidification and re-drying process. Both sets of data suggested that there
was a small change in their distributions. However, there was practically no particle measured in the DMA 2 for the 60 nm pre-selected dry particles which means that small particles may have evaporated before they entered the DMA.

**Figure 22.** Size distribution of pimelic acid particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 130 nm before entering the humidification process. There are 2 modes and the later mode is considered to be noise. The mode (averaged from all scans) is 108 nm.
Figure 23. Size distribution of pimelic acid particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 210 nm before entering the humidification process. There are 2 modes and the later mode is considered to be noise. The mode (averaged from all scans) is 188 nm.

AFM images and profile graphs of pimelic acid particles in the dry and DWD conditions are shown in Figure 24 and 25 respectively. Both sets of images show round and thin disk-shape particles. This result suggests that pimelic acid crystalizes into only one type of particles. There is not enough evidence to conclude if pimelic acid only has a single morphology or if we were only able to collect one of them.
**Figure 24.** AFM image and profile graphs of selected Pimelic Acid particles in dry condition (<10% RH). The image and the profile graphs show round thin disk-shape particles.
Figure 25. AFM image and profile graphs of selected Pimelic Acid particles in DWD condition (<10% RH then >85% RH then <10% RH). The image and the profile graphs show round thin disk-shape particles.
3. **Amino acids and inorganic compounds**

The second and third sets of chemicals that were investigated in this study were amino acids (glutamic acid and leucine) and inorganic compounds (calcium chloride, ammonium chloride, and ammonium nitrate). Some of their physical properties are listed in Table 3.
Table 3. Physical properties of investigated chemical species

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>MW</th>
<th>Melting Point, °C</th>
<th>Boiling Point, °C</th>
<th>Density 25°C, g/cm³</th>
<th>Vapor Pressure, Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glutamic Acid</td>
<td><a href="COOH">CHNH2(CH2)2</a>2</td>
<td>147.13</td>
<td>199</td>
<td>n.a</td>
<td>1.46</td>
<td>3.6E-5, 25°C</td>
</tr>
<tr>
<td>L - Leucine</td>
<td>(CH₃)₂CHCH₂CH(NH₂)COOH</td>
<td>131.17</td>
<td>295</td>
<td>sublimes</td>
<td>1.29</td>
<td>1.59E-8, 25°C</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>CaCl₂</td>
<td>110.983</td>
<td>772</td>
<td>&gt;1600</td>
<td>2.15</td>
<td>1.333, 20°C</td>
</tr>
<tr>
<td>Ammonium Chloride</td>
<td>NH₄Cl</td>
<td>53.50</td>
<td>350</td>
<td>520</td>
<td>1.519</td>
<td>133.3, 160°C</td>
</tr>
<tr>
<td>Ammonium Nitrate</td>
<td>NH₄NO₃</td>
<td>80.05</td>
<td>169.6</td>
<td>210</td>
<td>1.72</td>
<td>1900</td>
</tr>
</tbody>
</table>

a Perry’s Chemical Engineering Handbook, 7th ed.

b The Merck Index, 12th ed.

c Booth et al., 2010.

d Lähde, A. et al., 2009.


f Brandner J. D. et al., 1962.
a) Glutamic Acid

Glutamic acid was investigated using the same procedure as the dicarboxylic acids. Dry particles were sent through the DMA 2 to scan for their size distribution. In addition, they were also humidified and re-dried before being sent to the DMA 2 to measure for their size again. Their normalized size distributions are shown in Figure 26. As seen, the DWD distribution overlaps with the dry distribution which suggests that the particles have the same morphology regardless of the drying rate. However, AFM images of particles collected from the dry and DWD conditions did not confirm the results (Figure 27 and 28). The AFM image of dry particles shows thin cylindrical plate-like particles while the AFM image of DWD particles show some irregular shaped particles.
Figure 26. Normalized size distributions of glutamic acid particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 99.0 nm and 116.3 nm respectively.
Figure 27. AFM image and profile graphs of selected glutamic acid particles in Dry condition (<10% RH). The image and profile graph show mostly thin cylindrical plate-like particles.
Figure 28. AFM image and profile graphs of selected glutamic acid particles in DWD condition (<10% RH then >85% RH then <10% RH). The image and the profile graph show irregular shaped particles.
b) L – Leucine

Size distributions of L-leucine in dry and DWD conditions are shown in Figure 29. As seen in the figure, the DWD distribution is contained within the dry distribution which indicated that particles did not grow bigger in the second drying process. However, a portion of smaller particles were lost in the process which explains why the mode (averaged from all scans) of the DWD distribution became larger. To testify this result, the DMA 1 was used to pre-select a size before sending the dry particles to the humidification and re-drying process. Then their size distributions were measured again in the DMA 2. Figure 30, 31 and 32 show size distributions of pre-selected 40 nm, 80 nm and 300 nm dry particles after they went through the humidification and re-drying process. All three sets of data concluded that there was no change in their distributions.
Figure 29. Size distribution of L-leucine particles measured in dry condition (<10% RH) (blue line) and DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 139 nm and 179 nm respectively.
Figure 30. Size distribution of L-leucine particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 40 nm before entering the humidification process. The mode (averaged from all scans) is 37.8 nm.
Figure 31. Size distribution of L-leucine particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 80 nm before entering the humidification process. There are 2 modes and the later mode is considered to be noise. The mode (averaged from all scans) is 75.6 nm.
Figure 32. Size distribution of L-leucine particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 300 nm before entering the humidification process. There are 2 modes and the later modal is considered to be noise. The mode (averaged from all scans) is 282 nm.

AFM images and profile graphs of L-leucine particles in dry and DWD conditions are shown in Figure 33 and 34 respectively. Both sets of images show round disk-like particles which confirm the result of the SMPS distribution.
Figure 33. AFM image and profile graphs of selected leucine particles in dry condition (<10% RH). The image shows round disk-like particles.
Figure 34. AFM image and profile graphs of selected leucine particles in DWD condition (≤10% RH then >85% RH then ≤10% RH). The image shows some uneven round disk-like particles.
c) Calcium Chloride

Normalized size distributions of CaCl$_2$ in dry and DWD conditions are shown in Figure 35. As seen in the figure, the DWD distribution is slightly to the right of the dry distribution which indicated that the particles grew slightly bigger in the slow drying process. To testify this result, the DMA 1 was used to pre-select a size before sending the dry particles to the humidification and re-drying process. Then their size distributions were measured again in the DMA 2. Figure 36 and 37 show size distributions of pre-selected 50 nm and 140 nm dry particles after they went through the humidification and re-drying process. Both sets of data concluded that there was no change in their distributions. In addition, AFM images of particles collected from the dry and DWD conditions also confirm the result and are included in Appendix C.
Figure 35. Normalized size distributions of calcium chloride particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 76.9 nm and 102 nm respectively.
Figure 36. Size distribution of CaCl₂ particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 50 nm before entering the humidification process. There are 2 modes and the later mode is considered to be noise. The mode (averaged from all scans) is 50 nm.
Figure 37. Size distribution of CaCl$_2$ particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 140 nm before entering the humidification process. There are 2 modes and the later mode is considered to be noise. The mode (averaged from all scans) is 137 nm.
d) *Ammonium Chloride*

Normalized size distributions of NH$_4$Cl in dry and DWD conditions are shown in Figure 38. As seen in the figure, the DWD distribution overlaps with the dry distribution which suggests that the particles have the same morphology regardless of the drying rate. To verify this result, the DMA 1 was used to pre-select a size before sending the dry particles to the humidification and re-drying process. Then their size distributions were measured again in the DMA 2. Figure 39 shows size distributions of pre-selected 150 nm dry particles after they went through the humidification and re-drying process. The mode (averaged from all scans) of the distribution is 120 nm. However, there was practically no particle measured in the DMA 2 for the 50 nm pre-selected dry particles which explains why the mode (averaged from all scans) of the DWD distribution shifted slightly to the right. As shown in Table 3, the vapor pressure of NH$_4$Cl is sufficiently high; in the slow drying process, the small particles had evaporated while the big ones had shrunk a little. In addition, AFM images of particles collected from the dry and DWD conditions also confirm the result and are included in Appendix C.
Figure 38. Normalized size distributions of ammonium chloride particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 84.3 nm and 93.8 nm respectively.
Figure 39. Size distribution of NH₄Cl particles measured in DWD condition. The particles’ size was pre-selected using the DMA1 to be 150 nm before entering the humidification process. There are 2 modes and the later mode is considered to be noise. The mode (averaged from all scans) is 120 nm.
e) Ammonium Nitrate

Normalized size distributions and original size distributions of NH$_4$NO$_3$ in dry and DWD conditions are shown in Figure 40 and 41 respectively. As seen in Figure 41, the DWD distribution is contained within the Dry distribution which indicated that particles did not grow bigger in the second drying process. However, the bigger particles were significantly lost in the process which explains why the mode (averaged from all scans) of the DWD distribution shifted to the left. Since the particles that were lost were between 80 nm to 200 nm, they did not lose due to the effect of impaction. It was hypothesized that NH$_4$NO$_3$ had formed a different shape of crystals that have a smaller dimension that was detected by the DMA. This hypothesis was confirmed when the DMA 1 was used to pre-select a size and re-measured their distributions in the DMA 2. Figure 42 shows size distributions of pre-selected 60 nm dry particles after they went through the humidification and re-drying process. The data concluded that there was no change in size before and after the DWD process. However, there was practically no particle measured in the DMA 2 for the 120 nm pre-selected dry particles. It should be noted that NH$_4$NO$_3$ takes a longer time to reach steady state than any other chemicals that were studied in this project.
**Figure 40.** Normalized size distributions of NH₄NO₃ particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 79.1 nm and 36.5 nm respectively.
Figure 41. Size distribution of NH$_4$NO$_3$ particles measured in dry condition (<10% RH) (blue line) and DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 79.1 nm and 36.5 nm respectively.
Figure 42. Size distribution of NH$_4$NO$_3$ particles measured in DWD condition. The particles’ size was pre-selected using the DMA 1 to be 60 nm before entering the humidification process. The mode (averaged from all scans) is 54.7 nm.

The two-morphology hypothesis was also confirmed by the AFM images. As shown in Figure 43, the dry particles exhibit a plate-like shape with sharp edges. But in Figure 44, the DWD particles have disk shape with smooth edges. In other words, when NH$_4$NO$_3$ particles were dried the first time, they formed plate-like particles and when they were dried slowly the second time, they formed more like spherical particles.
Figure 43. AFM image and profile graphs of selected NH$_4$NO$_3$ particles in dry condition (<10% RH). The image shows some particles with sharp edges.
Figure 44. AFM image and profile graphs of selected NH$_4$NO$_3$ particles in DWD condition (<10% RH then >85% RH then <10% RH). The image shows some round-edge particles.
VII. Conclusions and Recommendations

Atmospheric aerosols have been known to impose various effects on the Earth’s climate as well as human health. They can reflect or absorb incoming solar radiation and directly affect the Earth’s radiation budget. They can also act as cloud condensation nuclei which alter the atmospheric conditions. How strong those effects are depends on several physical properties of particles such as size, morphology and hygroscopic properties. Furthermore, many industrial processes require recognizing those influences as well as being able to characterize their particles based on those properties. Moreover, studying particle morphology is a key factor in better controlling the synthesis and production of solid particles in many industries such as food, personal care, and pharmaceutical. Therefore, gaining a deeper knowledge about the particles’ size, morphology and hygroscopic properties in either case is crucial.

Other studies have been focusing on the difference in properties of particles at various RH conditions; however, prediction of whether or not their properties change once the particles are re-dried is not fully developed. In addition, atmospheric researchers have been assuming that particles’ morphology remains the same regardless of the drying rates. This thesis aimed to investigate the impact of different drying rates on the size and morphology of inorganics, amino acids and dicarboxylic acids (C3-C7) nanoparticles through the use of a scanning mobility particle spectrometer (SMPS) and an atomic force microscope (AFM). Several other techniques were used to conduct the investigations
including a humidified tandem differential mobility analyzer (HTDMA), an additional
differential mobility analyzer (DMA), and a PIXE impactor.

Each chemical species was generated using the atomizer from a solution of 1 g/L
and sent through a series of diffusion dryers. The particles at this stage had a RH of less
than 10% and were either collected in the PIXE impactor to be imaged under the AFM or
scanned for their size distributions in the scanning mobility particle spectrometer
(SMPS). This process is classified as the Dry experiment. In the Dry-Wet-Dry (DWD)
experiments, particles exiting the dryers went through two Nafion tubes (RH > 85%) and
re-dried in an additional dryer (RH < 10%) before entered the SMPS. In some cases
where the results needed to be confirmed, an additional differential mobility analyzer
(DMA) was connected between the first set of diffusion dryers and the humidification
apparatus. This DMA was used to pre-select a size for the dry particles before the
humidified modification.

Results revealed that the even dicarboxylic acids’ particles (C4 and C6) did not
change their size and morphology after the DWD process. However, the odd dicarboxylic
acids’ particles (C3, C5 and C7) exhibited a change in their size and morphology. This
confirmed our hypothesis that some chemical compounds formed two types of particles
in the slow drying process and the newly formed particles had a smaller dimension that
was detected by the DMA. To our surprise, glutaric acid (C5) formed two types of
particles in the fast drying process but reduced to one morphology in the slow drying
process. It was thought that these odd behaviors were due either to their high vapor
pressures or to specific factors of the drying process/rate.
Results of both amino acids (glutamic acid and L-leucine) showed that their size did not change after the humidification and re-drying process. However, AFM images of glutamic acid showed some changes in their morphology. AFM images of L-leucine confirmed the results of their size distributions. In addition, CaCl₂ and NH₄Cl exhibited no change in their size and morphology as well. Finally, results of NH₄NO₃ indicated that the particles might have crystallized into two forms depending on the drying rates.

While the results of this research help propose mechanisms by which atmospheric particles grow or crystallize after different RH cycles, additional works should be done to further understand the interaction of water and particles and to extend our knowledge of the effects of aerosol particles on the global climate. Particularly, more organic compounds should be investigated as their concentrations contribute significantly to the total concentration of particles in the atmosphere and their characteristics are not well understood. Higher carbon-number dicarboxylic acids should be extended in future studies to compare with the results of this thesis. Secondly, mixtures of organics and inorganics-organics should also be studied as their internal interactions might affect their interactions with water. Moreover, different cycles of humidification should be designed and applied to future projects to better imitate the actual atmospheric conditions. In addition, the humidification chamber should be modified to limit the loss of particles. Finally, a better method to collect nanoparticles than the PIXE impactor is necessary in future studies as the particles were under a great impaction pressure in the PIXE and their morphology might have altered.
VIII. References


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Appendix A. Preliminary Results and Discussion

Preliminary experiments were conducted to investigate two main objectives. The first objective was to validate the method of measuring temperature and RH over time as well as the ability of humidifying the aerosol stream by the Nafion tube. The second objective was to examine the size and morphology of aerosol particles before and after the humidified process.

1. Validation of apparatus set-up

In order to achieve the first objective of validating the apparatus, four investigations were conducted. The experimental apparatus was described in the previous section. For those preliminary experiments, NaCl was chosen to be investigated and all initial NaCl solutions had a concentration of 1g/L using the ultra-pure water obtained from Millipore water purification system for the solvent.

The first investigation was to confirm the temperature and RH of the dry stream. The NaCl aerosol particle stream, after passing through the diffusion dryer, was sent directly to the reaction chamber to verify its temperature and RH condition. The Vaisala meter recorded the stream constant temperatures at 22.54°C ± 0.18°C over a period of 10.5 minutes. The percent RHs are shown in Figure A.45 from the time before feeding the dry stream in until 10 minutes after. The RH reached steady state at 7.54% ± 0.2% in about 5 minutes.
As previously discussed, the apparatus was also constructed to split the dry stream of aerosol particles into 2 streams: the dry and the wet streams. In the second investigation, only the wet stream was fed into the reaction chamber to measure its temperature and RH condition over time. The constant temperature over 10.85 minutes was recorded as $23.5 \pm 0.15^\circ C$ and the percent RHs are shown in Figure A.46. The system reached steady state in less than 6 minutes. The highest percent RH recorded was $89.07\%$ and the average was $88.79\% \pm 0.28\%$.
Figure A.46. Percent RH over time recorded before and after feeding the wet aerosol stream into the reaction chamber

The third investigation was to verify the temperature and RH of the heated wet stream. It is important to mention that even though the stream was identified as the heated wet stream, the aerosol particle stream itself was never heated, only the water cycling in the Nafion tube was heated in a separated water bath. Figure A.47 shows the recorded percent RHs over time for the wet aerosol stream while the water bath temperature was set to rise continuously to 40°C. Temperatures of the wet aerosol stream were also documented over 17.23 minutes. The particle stream temperature was 24.54°C and the temperature was only fluctuated ± 0.39°C. As seen in Figure 48, the percent RHs continuously rose up to a maximum value of 93.86%.
Figure A.47. Percent RH over time recorded for the wet aerosol stream while the water cycling the Nafion tube was heated

Finally, an examination on the temperature and RH condition was conducted when both the dry and the wet aerosol streams were opened. The constant temperature was recorded as 23.17°C ± 0.08°C. The percent RHs are shown in Figure A.48 and averaged 13.33% ± 0.16%. It was suspected that the aerosols flew more freely in the dry line than the wet line since the wet pathway was a lot smaller than the dry way; therefore, the RH stayed relatively dry.
2. **Size and Morphology of Particles**

Although the primary focus of this research in the longer term is to investigate the size and morphology of nanoparticles, a preliminary test was done on micron scaled NaCl particles. The micron particles were analyzed under a scanning electron microscope (SEM) for their size and morphology. The results were then compared with the images analyzed under an atomic force microscope (AFM) for nanoparticles. In both cases, the NaCl initial solutions had a concentration of 1 g/L and all particles were collected on 12 mm steel disks which were coated with gold to view under the SEM or covered with mica discs to view under the AFM. Additionally, five stages of the PIXE impactor were used in both experiments including L1, 1, 3, 5 and 7. Stages that collected larger particles were
used for the SEM imaging (stage 5 and 7) while the smaller stages were used for AFM imaging.

**a) Scanning Electron Microscopy (SEM) images**

Images A and B in Figure A.49 were taken from stage 5 of the PIXE impactor of NaCl particles using only the dry stream. As shown in Figure A.49, the particles have relatively equivalent size as well as identical shape. The majority of particles is approximately 2-3 \( \mu \text{m} \) and has a shape of cubes. Additionally, there were clusters of particles throughout the sample plate suggesting that future experiments should reduce the collecting time.

![Figure A.49. SEM images of NaCl particles collected from the dry line](image)

**Figure A.49.** SEM images of NaCl particles collected from the dry line
The SEM images A and B in Figure A.50 were also taken from stage 5 of the PIXE impactor using the same initial NaCl solution and only allowing the wet stream through. As shown in Figure A.50, the NaCl particles were separated more than in the previous image. Nonetheless, the wet particles have similar size and shape as the dry particles. Moreover, the particles shape is no longer a perfect square although they are faceted. This result suggests that when the particles are humidified, their surfaces get dissolved by the water.

![SEM images of NaCl particles collected from the wet line](image)

**Figure A.50.** SEM images of NaCl particles collected from the wet line

**b) Atomic Force Microscopy (AFM) images**

Figure A.51, 52, and 53 are three AFM images of NaCl particles that were taken from stage L1 of the PIXE impactor allowing only the dry aerosol stream through. Figure A.51 shows the overview image of the particles. Figure A.52 displays profile graphs of a few NaCl particles to show their diameters and heights. Figure A.53 is a three
dimensional image of the particles. As seen in these images, the dry NaCl particles have various sizes and shapes. It was suggested that there might have been more than 1 layer of dry particles that were impacted on the mica disc. This would explain why the large particles have few humps in the profile graphs and the 3D image. Nonetheless, the dry particles are shown to have both straight and round edges. This result implies that the dry nanoparticles might hold 2 different shapes: sphere and cube.

Figure A.51. AFM image of NaCl particles collected from the dry line
Figure A.52. Profile graphs of selected NaCl dry particles

Figure A.53. 3D image of NaCl dry particles
Figure A.54, 55, and 56 are AFM images that were also taken from stage L1 of NaCl particles in this case using only the wet stream. Similar to the dry particles images, figure A.54 shows the overview capture of the particles, figure A.55 plots the diameter vs height of a few selected particles, and figure A.56 presents a three dimensional image of the particles. As seen from the overview image, the nanoparticles have a more uniform size and shape than the dry particles. These particles have a diameter of approximately 1\( \mu \)m and a height of 0.33 \( \mu \)m. These dimensions are similar to those of the dry particles. This result was not what was expected as the wet particles should have a wider bottom and a shorter height. Moreover, they have straight edge tops and are more round in the bottoms.

![AFM image of NaCl particles collected from the wet line](image)

**Figure A.54.** AFM image of NaCl particles collected from the wet line
Figure A.55. Profile graphs of selected NaCl wet particles

Figure A.56. 3D image of NaCl wet particles

Figure A.57, 58, and 59 were also taken from L1 stage of the PIXE impactor having both the dry line and the wet line opened. The three images were analyzed and organized in the same fashion as the previous discussions. The first overview image
(Figure A.57) shows that the particles possess different sizes and there might have been more than 1 layer of particles on the mica disc similar to the previous dry particles images. Also, those mixed particles are nearly half the diameter and height of the dry and wet particles. The average diameter is approximately 0.5 μm and the average height is near 0.2 μm. This indicates that the wet particles might have dried out and shrank when they met with the dry stream. Similarly to the dry and wet particles, the mixed particles have some straight edges and some round edges.

Figure A.57. AFM image of NaCl particles collected from the dry and wet lines mixed
Figure A.58. Profile graphs of selected NaCl dry and wet particles

Figure A.59. 3D image of NaCl dry and wet particles
Appendix B. Size Distributions of Studied Chemicals

Figure B.60. Size distribution of ammonium sulfate particles measured in dry condition (<10% RH) (blue line). Next, the particles were humidified to >85% RH then re-dried to <10% RH (DWD condition). Their distribution was measured again (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 81.9 nm and 94.4 nm respectively.
Figure B.61. Size distributions of succinic acid particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The mode (averaged from all scans) s of both distributions were measured using the scanning mobility particle spectrometry (SMPS). The modes (averaged from all scans) of both distributions are 94.8 nm and 90.5 nm respectively.
Figure B.62. Size distributions of adipic acid particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The mode (averaged from all scans) of both distributions were measured using the scanning mobility particle spectrometer (SMPS). The modes (averaged from all scans) of both distributions are 103.7 nm and 115.7 nm respectively.
Figure B.63. Size distributions of glutaric acid particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The mode (averaged from all scans) of the DWD distribution is 37.5 nm. The dry distribution has 2 modals at approximately 28 nm and 110 nm.
Figure B.64. Size distributions of glutamic acid particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The mode (averaged from all scans) of both distributions are 99.0 nm and 116.3 nm respectively.
Figure B.65. Size distributions of calcium chloride particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The mode (averaged from all scans) of both distributions are 76.9 nm and 102 nm respectively.
Figure B.66. Size distributions of ammonium chloride particles measured in dry condition (<10% RH) (blue line) and in DWD condition (red line). Both distributions were measured using the scanning mobility particle spectrometer (SMPS). The mode (averaged from all scans) s of both distributions are 84.3 nm and 93.8 nm respectively.
Appendix C. Atomic Force Microscopy Images and Profile Graphs of Studied Chemicals

**Figure C.67.** AFM image and profile graphs of selected NH$_4$SO$_4$ particles in Dry condition (<10% RH). The image and profile graph show mostly spherical particles.
Figure C.68. AFM image and profile graphs of selected NH$_4$SO$_4$ particles in DWD condition (<10% RH then >85% RH then <10% RH). The image and the profile graph show mostly spherical particles.
Figure C.69. AFM image and profile graphs of selected succinic acid particles in Dry condition (<10% RH). The image and profile graph show mostly spherical particles.
Figure C.70. AFM image and profile graphs of selected succinic acid particles in DWD condition (<10% RH then >85% RH then <10% RH). The image and the profile graph show mostly spherical particles.
Figure C.71. AFM image and profile graphs of selected adipic acid particles in Dry condition (<10% RH). The image and profile graph show mostly cylindrical plate-like particles.
Figure C.72. AFM image and profile graphs of selected adipic acid particles in DWD condition (<10% RH then >85% RH then <10% RH). The image and the profile graph show mostly cylindrical plate-like particles.
Figure C.73. AFM image and profile graphs of selected CaCl$_2$ particles in Dry condition (<10% RH). The image and profile graph show mostly spherical particles.
Figure C.74. AFM image and profile graphs of selected CaCl₂ particles in DWD condition (<10% RH then >85% RH then <10% RH). The image and the profile graph show mostly spherical particles.
Figure C.75. AFM image and profile graphs of selected NH₄Cl particles in Dry condition (<10% RH). The image and profile graph show mostly cylindrical plate-like particles.
Figure C.76. AFM image and profile graphs of selected NH$_4$Cl particles in DWD condition (<10% RH then >85% RH then <10% RH). The image and the profile graph show mostly cylindrical plate-like particles.