Chemical composition of atmospheric nanoparticles during nucleation events in Atlanta

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[1] We report the first direct, in situ measurements of the chemical composition of size-segregated atmospheric nanoparticles in the 6–15 nm diameter range. These measurements were made of ambient aerosol directly following nucleation events in Atlanta, Georgia, during the 2002 Aerosol Nucleation and Real-time Characterization Experiment (ANARChE). The recently developed Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) was used to make these measurements and featured a new inlet that delivers mass of charged and size-segregated nanoparticles at sufficiently high rates to enable analysis at a typical time resolution of 10 min. Measurements in both the positive and negative ion spectra revealed that particles formed recently from nucleation events have enhanced concentrations of ammonium and sulfate and that to within the uncertainty of our measurements, ammonium sulfate could account for all of the sampled nanoparticle mass. No other compounds were detected in the particles during these events. Concurrent measurements of particle hygroscopicity and volatility, made using a Nanometer Tandem Differential Mobility Analyzer, support the conclusion that ammonium and sulfate are primary components of these newly formed particles.


1. Introduction

[2] Nucleation is an important source of atmospheric particles in a variety of settings [Kulmala et al., 2004]. Once formed, particles can grow quickly to participate in a number of important atmospheric processes such as heterogeneous chemistry, cloud formation, precipitation, and the scattering and absorption of solar radiation. Characterizing the compounds responsible for growth is important for understanding the links between nucleation and the processes mentioned above. In addition, knowledge of the composition of atmospheric nanoparticles (sub-50 nm diameter) may aid in the assessment of their health effects, which presently are thought to be deleterious [Oberdörster et al., 1995].

[3] Most information on the chemical composition of particles formed following nucleation has been obtained using offline techniques in which particles are collected on a substrate for later laboratory analysis, or indirect techniques in which the chemical composition is inferred by measuring some other property. One recent example of the use of offline microanalytical techniques has been reported in the study of recently formed particles in a coastal setting. That study observed both iodine and sulfur in particles with diameter below 10 nm [Mäkelä et al., 2002], suggesting that biogenic iodine species emitted from seaweeds may be responsible for new particle formation and/or growth. In another example, 5–30 nm diameter particles from a boreal forest in Hyytiälä, Finland, were collected using a low-pressure impactor and analyzed using ion chromatography [Mäkelä et al., 2001]. That study found that newly formed particles were enriched with dimethylamine, which suggested a biogenic origin. In the latter study, a 24-hour sampling time was required to collect sufficient material for analysis. Another indirect approach, in which the growth characteristics of particles in a condensation particle counter was investigated using the pulse height analysis technique [Saros et al., 1996], was used to study new particle formation at Hyytiälä. In that investigation the authors concluded that these particles were composed primarily of organic acids [O’Dowd et al., 2002].

[4] Information about nanoparticle composition has also been inferred indirectly from measurements of hygroscop-
icity or volatility of size-classified particles [e.g., Sakurai et al., 2003]. One notable example of this used to study aerosol formed directly following a nucleation event is the subject of a companion paper in this issue by Sakurai et al. [2005], the results of which will be presented and discussed in sections 5 and 6, respectively, in relation to our measurements of chemical composition. That instrument, called a Nano TDMA, exposes size-classified 3–30 nm diameter particles to high humidity (usually 90% RH) or high temperature (100–150°C). A particle size distribution measurement is then made following this exposure to determine the degree to which the particles changed size. For example, an increase in the size of particles that are exposed to high humidity means that particles are hygroscopic, and is consistent with particles composed of inorganic ions such as ammonium sulfate and sodium chloride.

The first direct, real-time measurements of the chemical composition of ambient ultrafine particles following a nucleation event was reported recently by Zhang et al. [2004]. In those measurements made with an Aerosol Mass Spectrometer [Jayne et al., 2000] following nucleation events in Pittsburgh, particles in the 18–33 nm diameter range were first composed of sulfate, and then after 10–40 min began to include ammonium, organics, and to a lesser degree, nitrate. In that setting, secondary organics contributed significantly to the growth of ultrafine particles in the afternoon when photochemistry was most active. Similar measurements using the Aerosol Mass Spectrometer have been made in the boreal forest at Hyytiälä. In that study, measurements of sub-100 nm particles resulting from the growth over several hours of the nucleation event showed their mass to be principally, if not entirely, composed of organic species [Allan et al., 2003].

We report here size-segregated chemical composition measurements of 6–15 nm diameter particles directly following nucleation events. These were performed using the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) at the Jefferson Street site in midtown Atlanta during the 2002 Aerosol Nucleation and Real-time Characterization Experiment (ANARChE). The purpose of ANARChE was to investigate both nucleation and ultrafine particle growth in the atmosphere immediately following the formation of new particles by nucleation. A table summarizing the ANARChE measurements most pertinent to the study of nucleation and growth is given in a companion paper in this issue [McMurry et al., 2005, Table 1].

2. Instrument

The TDCIMS is capable of performing measurements of the molecular composition of 5–20 nm diameter particles in near real-time and with a time resolution of less than 20 min. A schematic of the instrument is shown in Figure 1, and details on the operation of the instrument can be found in two recent journal articles [Smith et al., 2004; Voisin et al., 2003]. Briefly, sampled particles are first charged and, optionally, size selected before being collected by electro-
static deposition on a metal filament. Once a sufficient mass of nanoparticles is collected the filament is transferred into the chemical ionization region of a mass spectrometer where it is resistively heated to evaporate the deposited particles. The desorbed molecules are then chemically ionized by reactions with $H_2O^+(H_2O)_n$ and $O_2^+(H_2O)_m$ where $n$ and $m$ are the range of 1–6. Once ionized, the species are first declustered in a drift cell and then mass analyzed using a triple quadrupole mass spectrometer (Extem Corp.).

Recently, the authors reported the first measurements of chemical composition of sub-20 nm diameter atmospheric particles using the TDCIMS. In those investigations, which focused on ambient particles that made up the low-diameter tail of the accumulation mode, the composition was obtained for a mass- and sampling efficiency-weighted integration over the diameter range of 6–20 nm. In that study, sulfate, nitrate and ammonium were the dominant compounds in the particles, along with other compounds that could not be identified, but were presumed to be organic [Smith et al., 2004].

In using the TDCIMS for studying new particle formation and the compounds responsible for their growth, size selectivity is essential in order to exclude primary particles (such as those emitted by combustion sources) and more aged secondary particles. Although this can be accomplished to a certain degree by the size-dependent collection efficiency of the TDCIMS [Smith et al., 2004], a more effective means to do this is by adding a differential mobility analyzer (DMA [Knutson and Whitby, 1975]) between the unipolar charger and the electrostatic precipitator inlet. This must be done with due consideration to both particle mass required for analysis and the desired measurement time resolution.

To address the need for high sample flows of size-segregated, charged nanoparticles, the current TDCIMS features a parallel configuration of three aerosol charger/DMA pairs. This subsystem, called the nanoparticle delivery system, consists of three unipolar chargers and three Nanometer Differential Mobility Analyzers (Nano DMAs) assembled together in three separate subunits and operated in parallel. Figure 1 shows the arrangement. The unipolar chargers, based on the design by Chen and Pui [1999], exhibit high charging efficiency and high throughput for particles in the size range of 3–50 nm. Laboratory tests have shown that the probability of sub-20 nm particles acquiring more than one charge as they pass through the unipolar charger is negligible [Ghimire, 2004]. The Nano DMAs are commercial instruments (TSI, Inc., model 3080N), based on the design of Chen et al. [1998]. Nitrogen was used as the sheath gas for each Nano DMA in order to protect the sample particles and the TDCIMS collection filament from contamination by gases that would be present in filtered ambient air. A control valve and vacuum pump were used to control the Nano DMA excess flow. The Nano DMAs are operated in the underpressure mode, in which the sample flow is drawn in by a vacuum pump/flow controller combination situated at the exhaust port of the TDCIMS inlet. The manifold that combines the sample flows from each of the three Nano DMAs is designed to equalize the sample flows in each Nano DMA. An orifice located between the Nano DMA and the unipolar charger is drilled to a diameter that passively controls the ratio of sheath and inlet flows. The excess flows were monitored using inline laminar elements and differential pressure meters, and the sheath and aerosol flows were checked at least once per day using a Gilibrator flow calibrator (Sensidyne, Inc.). Throughout the study these flows were observed to be constant.

For this study the Nano DMAs were operated unconventionally, as can be seen from the flow rates given in Table 1. In order to achieve sufficiently high delivery rates of size-selected nanoparticle mass, the flow rate of mobility-classified particles from each Nano DMA was maintained at 11.2 lpm. Atmospheric aerosol was sampled at 4.5 lpm, and the total flow rate for each DMA was 19.5 lpm. The ranges of particle diameters transmitted through the DMA when 101 V and 453 V are applied are represented by the transfer functions plotted in Figure 2. To generate these, size-resolved $(NH_4)_2SO_4$ particles were produced with an electrospray aerosol generator (TSI, Inc., model 3480) and introduced into the Nano DMAs, which were operating in parallel under the operating conditions described above. A condensation particle counter (TSI, Inc., model 3025) was used to characterize the concentration of particles passing into the DMAs as well as the concentration at the outlet of the DMAs. In the following discussion these two size classes shown in Figure 2 will be represented by their volume mean diameters, 8 nm and 13 nm, respectively. The width of these distributions are in reasonable agreement with the predicted widths of 2.7 nm and 4.4 nm, respectively, on the basis of DMA transfer functions derived by Knutson and Whitby [1975]. The range of particle sizes sampled in this way is significantly broader than is typically obtained from DMAs when operated

### Table 1. Nano DMA Operating Flows for the Current Study

<table>
<thead>
<tr>
<th>Description</th>
<th>Flow Rate, 1 min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosol in ($q_a$)</td>
<td>4.5</td>
</tr>
<tr>
<td>Sheath air ($q_s$)</td>
<td>15</td>
</tr>
<tr>
<td>Sample ($q_g$)</td>
<td>11.17</td>
</tr>
<tr>
<td>Excess air ($q_m$)</td>
<td>8.33</td>
</tr>
</tbody>
</table>

![Figure 2. Nano DMA transfer functions (i.e., size-resolved transmission efficiencies) for the 8 nm and 13 nm diameter particle classes using the flows presented in Table 1.](image-url)
with lower ratios of aerosol to sheath air flow rates, but still sufficiently narrow for our purposes.

3. Experiment

[12] The TDCIMS acquired data during the period 13–30 August, during which time nine nucleation events were observed [Sakurai et al., 2005, Table 2]. Measurements were usually performed on the 13 nm particle class over a time interval of 5–20 min, depending on the ambient concentration. When higher concentrations of sub-10 nm diameter particles were encountered as a result of new particle formation, the selected diameter was usually lowered to 8 nm to observe any size-dependent changes in particle composition. During other measurement periods, the selected particle diameter was kept constant to focus on the relative change in concentration over the course of new particle formation and growth. Only ions of a single polarity were studied during an event because of the time required to change the ion polarity of the TDCIMS.

[13] Calibration tests were also performed on site during the operational period. These tests used (NH₄)₂SO₄ particles generated by the electrospray aerosol generator and were performed using all combinations of flows, voltages, and filament positions that were used in the ambient measurements. Thus the results of these calibration runs could be directly compared to the ambient measurements in order to quantify the TDCIMS results. That procedure, as well as the method used to estimate the total particulate volume collected for analysis, are presented in the following section.

4. Data Analysis

[14] During operation, 2–6 ion species of the same polarity were monitored at any given time. Usually one of these ion measurements was performed with the quadrupole mass spectrometer in RF-only mode, in which the mass spectrometer was operated in RF-only mode, in which the mass spectrometer in RF-only mode, in which the mass spectrometer was operated in RF-only mode, in which the mass spectrometer was operated in RF-only mode. Since the declustered H₂O⁺ (in the positive ion spectra) and the declustered H₃O⁺ (in the negative ion spectra) were monitored. The major reagent ions, represented by the declustered H₂O⁺ (in the positive ion spectra) and the declustered H₃O⁺ (in the negative ion spectra), were also monitored. The remaining ions that were monitored included those observed in nanoparticles from our measurements in Boulder, Colorado (e.g., NH₄⁺, HSO₄⁻, and NO₃⁻) [Smith et al., 2004], as well amines and oxygenated organics that are suspected to be in ambient particles and have been successfully identified in laboratory tests using the TDCIMS: dimethylamine, pinic acid, pinonaldehyde, and the ethyl cation (29 Th, a commonly observed fragment ion from the thermal decomposition of larger organic compounds). At times we also systematically scanned over the mass-to-charge range of 15–100 Th in an attempt to find compounds that have not previously been identified in earlier investigations.

[15] Smith et al. [2004] describe the procedures used for operating the TDCIMS and for processing the raw data. To summarize, the concentration of species A in the sample can be represented as a value, \( \chi_{A,\text{samp}} \), which is defined as the ratio of the ion abundance of species A to that of the reagent ion, integrated over the time during which the sample is thermally desorbed. The “species A partial volume,” \( V_A \), is the total volume of pure, single component particles that would give the same signal as that observed for the ambient particulate sample. \( V_A \) is found by dividing \( \chi_{A,\text{samp}} \) by \( \chi_{A,\text{cal}} V_{\text{cal}} \), the latter being the volume-normalized ratio of species A obtained with pure, single component calibration particles to that of the reagent ion, analyzed under identical operating conditions:

\[
V_A = \frac{\chi_{A,\text{samp}}}{\chi_{A,\text{cal}} V_{\text{cal}}} = \frac{\chi_{A,\text{samp}}}{\chi_{A,\text{cal}}} V_{\text{cal}}. \tag{1}
\]

where \( V_{\text{cal}} \) is the collected particulate volume for the calibration tests. One final value, the “species A volume fraction” is used in the current analysis to quantify the composition of ambient particles, and is defined by the ratio, \( V_A/V_{\text{sam}} \):

\[
\frac{V_A}{V_{\text{sam}}} = \frac{\chi_{A,\text{samp}}}{\chi_{A,\text{cal}} V_{\text{sam}}}. \tag{2}
\]

The species A volume fraction can be used to answer the question: “On the basis of the measured species A ion signal, how much of the ambient particles can be described as pure, single component particulate species A?”

[16] The remainder of the discussion is devoted to the calculation of the species A volume fraction (equation (2)). This is not discussed by Smith et al. [2004], since the current study is the first to employ Nano DMAs to size-classify particles prior to analysis. We start by expressing the rate at which particulate volume is collected by the filament as the difference between the rates at which particulate volume passes through the exhaust port before collection (\( \dot{V}_{\text{bkgd}} \)) and during collection (\( \dot{V}_{\text{coll}} \)), divided by the average efficiency (\( \bar{\epsilon} \)) with which particles travel from the collection filament to the exhaust port:

\[
\dot{V}_{\text{fil}} = \left[ \dot{V}_{\text{bkgd}} - \dot{V}_{\text{coll}} \right]/\bar{\epsilon}. \tag{3}
\]

Equation (3) is a good approximation in the current study, since \( \bar{\epsilon} \) has been found to be invariant over the range of particle diameters transmitted by the Nano DMAs for a given size class. The collected particulate volume is calculated from equation (4), where \( t \) is the total collection time:

\[
V = \int_0^t \dot{V}_{\text{fil}} dt = \frac{1}{\bar{\epsilon}} \int_0^t \left[ \dot{V}_{\text{bkgd}} - \dot{V}_{\text{coll}} \right] dt. \tag{4}
\]

Applying this result to equation (2), the species A volume ratio is given as:

\[
\frac{V_A}{V_{\text{sam}}} = \frac{\chi_{A,\text{samp}}}{\chi_{A,\text{cal}}} \frac{\int_0^t \left[ \dot{V}_{\text{bkgd}} - \dot{V}_{\text{coll}} \right] dt}{\int_0^t \left[ \dot{V}_{\text{bkgd}} - \dot{V}_{\text{coll}} \right] dt}. \tag{5}
\]
The two particulate volume rates, $\dot{V}_{\text{ech}}^{\text{bkgd}}$ and $\dot{V}_{\text{ech}}^{\text{coll}}$, are defined as follows:

$$
\dot{V}_{\text{ech}}^{\text{bkgd}} = Q_{\text{amp}} \int_0^\infty n(D_p) \phi(D_p) \beta_1(D_p) \Omega(D_p) \beta_2(D_p) \frac{\pi D_p^3}{6} dD_p,
$$

(6a)

$$
\dot{V}_{\text{ech}}^{\text{coll}} = Q_{\text{amp}} \int_0^\infty n(D_p) \phi(D_p) \beta_1(D_p) \Omega(D_p) [1 - \alpha(D_p)] \beta_2(D_p) \frac{\pi D_p^3}{6} dD_p.
$$

(6b)

$D_p$: particle diameter

$Q_{\text{amp}}$: sample flow rate

$n(D_p)$: sampled particle size distribution

$\phi(D_p)$: extrinsic charging efficiency of the unipolar charger (includes the transmission efficiency of the chargers)

$\alpha(D_p)$: particle collection efficiency

$\beta_1(D_p)$: transmission efficiency of tubing between inlet and collection filament (does not include transmission of the Nano DMA).

$\beta_2(D_p)$: transmission efficiency between collection filament and exhaust port.

$\Omega(D_p)$: Nano DMA transfer function

[17] The factor $\phi(D_p)\beta_1(D_p)\Omega(D_p)\beta_2(D_p)$ is the overall, size-resolved efficiency by which particles are transferred through the nanoparticle delivery system, the electrostatic precipitator of the TDCIMS, and out the exhaust port. To determine this product, we introduced a range of size-resolved, laboratory-generated (NH$_4$)$_2$SO$_4$ particles of known number concentration into the inlet of one of the unipolar charger/Nano DMA units (with the other two units operating but with particle filters attached to their inlets). The Nano DMAs were then set to the voltage corresponding to the desired sampled diameter and the number concentration was recorded over the range of diameters spanned by the size class as particles exited the exhaust port of the TDCIMS (refer to Figure 1 for an instrument schematic). The ratio of this concentration to that at the inlet to the unipolar charger is equal to the above product. The factor $\phi(D_p)\beta_1(D_p)\Omega(D_p)\beta_2(D_p)$ is the size-resolved efficiency by which particles are transferred through the system while the collection voltage is applied to the filament, and is calculated in the same manner. Since particles that exit the unipolar charger are in equilibrium with the ions generated within the charger, the resulting particulate charge distribution is independent of the initial particle charge distribution [Ghimire, 2004]. Thus the instrument response to calibration particles generated by the electrospray aerosol generator is representative of that for ambient particles.

[18] In order to obtain $n(D_p)$ we used continuous 3 nm to 2 μm diameter ambient particle size distributions taken during ANARCHe from the Particle Size Distribution (PSD) system. This instrument is described in a companion paper [Sakurai et al., 2005], and is similar to the system described by Woo et al. [2001]. The PSD instrument acquires number distributions over a broad size range by combining measurements from three instruments: one nanometer and one regular scanning mobility particle sizer (based on a TSI, Inc. model 3080N Nano DMA and a TSI, Inc. model 3081 DMA, respectively), and one optical particle counter (PMS, Inc. LASAIR model 1002). The PSD instrument acquired a size distribution every 2.5 min, which is high temporal resolution for most applications but proved insufficient for capturing the fluctuations in the number concentration of the smallest particles in the distribution. For example, frequently during new particle formation events the particle counter located at the exhaust port of the TDCIMS recorded fluctuations in particle number density at time intervals of 1–10 s. In order to account for rapid fluctuations in the particle size distribution, we interpolated the distributions for the period between PSD acquisitions, and scaled the interpolated values by the total number concentration detected at high time resolution (1 s) by the exhaust port particle counter. This allowed us to obtain values for $\dot{V}_{\text{ech}}^{\text{bkgd}}$ and $\dot{V}_{\text{ech}}^{\text{coll}}$ at time intervals of 1 s. We performed an uncertainty analysis for the collected particulate volume by propagating the observed errors of all factors in equations (6a) and (6b). This uncertainty varies from 10–50% as a function of size distribution, where the 30–50% uncertainties correspond to instances where very low particulate volumes were collected.

5. Results

[19] Table 2 presents the major new particle formation events observed while TDCIMS measurements were carried out and includes a summary of the observations of the TDCIMS for the days when the measurements were quantifiable. On the days for which no volume ratios are listed, the TDCIMS clearly detected the presence of the ions listed but operated under conditions that differed from those used to generate $X^{\text{ech}}$, thus making it impossible to calculate the volume ratio. In the table, new particle formation events are designated as either “plume impact” (localized in space and time) or “regional event” (taking place over a larger-scale air mass), consistent with the notation of Kulmala et al. [2004].

[20] As Table 2 shows, the TDCIMS measurements found that the only compounds present in measurable quantities in the 8 and 13 nm diameter particle size classes were ammonium (in the positive ion spectrum) and sulfate (appearing as HSO$_4^-$ in the negative ion spectrum). The observation that only ammonium and sulfate are seen in our TDCIMS measurements arises in spite of a considerable effort placed in searching for other compounds in the particles during these events, and contrast with our earlier measurements made of sub-20 nm diameter accumulation mode particles in Boulder, Colorado [Smith et al., 2004]. In that study, numerous ion species in both the positive and negative spectra were observed with peak amplitudes that were factors of ten or more smaller than those associated with the major species: NH$_3$+, HSO$_4^-$, and NO$_3^-$.

[21] For the five days for which quantifiable results were achieved, a closer examination reveals that the
observed compounds vary in their volume ratio during the measurement period, and that peak volume ratios are associated with peak particle concentrations that characterize nucleation events. These peaks are often delayed by 30 min to 2 hours after the onset of new particle formation. These observations are described in detail below.

5.1. Particulate Sulfate During New Particle Formation Events

[22] Figures 3 and 4 present data for two measurement periods in which sulfate was observed by the TDCIMS. The data for each day are presented in three plots: At the top is the continuous record of the particle size distribution, dN/dlogDp, measured by the PSD instrument, in the center is a plot of the particulate volume collected for analysis by the TDCIMS, and at the bottom is the record from the TDCIMS instrument, presented as the sulfate volume ratio, VHSO4/Vamp, as described above.

[23] Figure 3 shows a 9-hour period in which several aerosol plume impact events were superimposed upon a regional growth event on 23 August 2002. Figure 3b shows that most of the particulate volume seems to be associated with both the regional growth event (appearing in the 10–50 nm diameter range from 9:00 until approximately 14:30) and the several short-lived plume impacts from 10:10 to 12:45. During the period the TDCIMS collected and analyzed 13 nm diameter particles with a collection time of 15 min per sample (Figure 3c). The sulfate volume ratio prior to the plume impacts (9:17–10:02) averaged 0.12 ± 0.06. This ratio then began to increase after the first set of plume impact events, reaching a peak during the period 12:37–12:57 with an average value of 0.49 ± 0.25. Following this, the volume ratio fell back to an average value of 0.18 ± 0.17 for the period 14:00–17:00. During the measurement period the Nano TDMA characterized the hygroscopicity of 4 nm particles that were exposed to 90% RH. During the event these 4 nm diameter particles were hygroscopic, with a growth factor of 1.2 [Sakurai et al., 2005]. This observation is consistent with that of laboratory tests using pure ammonium sulfate aerosol.

[24] Since the Nano DMAs allow particles of a fairly broad size range to enter the instrument (with a ΔDp/Dp = 0.67, as shown in Figure 2), it’s often possible, particularly when monitoring the larger size class, to sample some of the small diameter tail of the more aged aerosol in addition to nucleation mode aerosol. This is clearly seen in Figures 3a and 3b, where the tail of the larger particle regional growth mode contributes to the collected particulate volume during the period 9:17–10:02. The consequence of this is that the collected particulate volume is not necessarily well correlated with ambient concentrations of sub-10 nm particles. This does not affect the measurements, since they are presented as “volume fractions” and are thus inherently volume normalized. However, as the data in Figure 3c show, the effect of sampling from these two modes is that the results favor the mode with the most mass, i.e., from the larger particle regional growth mode. The fact that sulfate volume fractions are low during this period suggests that nonsulfate compounds may be partially responsible for this larger diameter regional growth event. Furthermore, the time at which sulfate volume fraction peaks corresponds to relatively low amounts of collected particulate volume, suggesting that the large particle growth mode has passed outside the 13 nm size class so that the TDCIMS is preferentially sampling the particles formed by the plume impact events.

[25] Figure 4 shows a series of plume impact events that occurred during 13:38–15:15 on 25 August 2002. As the size distributions in Figure 4a show, these events were characterized by 3–10 nm diameter particle concentrations in the range of (5–33) × 10⁴ cm⁻³. Although we were not able to make a background measurement prior to the onset of these events, the measured volume ratio did start out relatively low for the 13 nm size class with a sulfate volume fraction of 0.60 ± 0.18 at 13:56. The next measurement at 14:17 corresponded to the peak in the volume fraction during that measurement period of 1.7 ± 0.5. This was followed by a decrease to values below 1 during the remaining plume impacts, which occurred at 14:30–15:30. The peak in the volume fraction occurs 39 min after the onset of new particle formation. During the entire measurement period the Nano TDMA characterized the volatility of 10 nm diameter particles that were heated at 100°C. Prior to the event the particles were slightly volatile (diameter decrease of 1–2 nm) and during the event they became nonvolatile (no diameter decrease or slight increase).
Again, this is consistent with the Nano TDMA’s response to pure ammonium sulfate aerosol.

5.2. Particulate Ammonium During New Particle Formation Events

Figures 5–7 present data from three days in which ammonium was observed in 6–15 nm diameter particles by the TDCIMS, with the data for each day presented in a similar manner to those of sulfate. During the measurement period of 11:00–18:00 on 17 August (Figure 5), a plume impact event was observed followed directly by a 1-hour period of growth of the size distribution (13:30–14:30). During the period prior to that plume impact event (11:03–13:07), the ammonium volume fraction for 13 nm diameter particles averaged 0.55 ± 0.17. The ammonium volume fraction for 13 nm particles peaked at around 15:00 and remained high with an average value of 1.4 ± 0.4 for the next 3 hours before it appeared to decrease somewhat after 17:30. Concurrent meteorological measurements show that the shift in ammonium volume fraction after 17:30 corresponded to a wind direction change from west (the predominant direction during most of the day) to east. The data are quite scattered following the new particle formation event, and uncertainty is quite large, which reflects the low volumes collected for analysis (Figure 5b). From 13:56 to 14:18 the TDCIMS analysis diameter was shifted between 8, 10, and 13 nm (Figure 5c). These measurements show no appreciable difference in ammonium concentration for particles in this size range. During the entire measurement period the Nano TDMA characterized the volatility of 8 nm diameter particles. During the event particles that were heated to 150 °C decreased in diameter by about 4 nm [Sakurai et al., 2005], which is consistent with the behavior of 8 nm diameter ammonium sulfate calibration particles.

Figure 3. Time series plots of (a) particle size distributions, (b) TDCIMS collected particulate volume, and (c) sulfate volume fractions directly following new particle formation events on 23 August 2002. Horizontal bars on each point in Figures 3b and 3c show TDCIMS collection period. Vertical dashed lines show time span for new particle formation event. The annotation in Figure 3b shows how the collected particulate volume may be influenced by the larger particle mode prior to 13:00.
Figure 6 shows a measurement period spanning the hours of 7:30 to 14:00 on 22 August 2002. The plot of the size distributions (Figure 6a) shows a plume impact event that took place at 8:45–9:00 and a regional growth event of 20–30 nm diameter particles over the period 9:30–10:45. During this period, the TDCIMS monitored 13 and 8 nm diameter particles, the latter during the period of most intense nanoparticle growth from 8:50 to 10:00. This period during the plume impact event is characterized by increasing levels of ammonium, reaching a peak in volume fraction (3.1 ± 0.8) during the period 9:25–10:01, before decreasing slightly just before 10:00. A discussion of the observation of volume fractions greater than 1 is presented in the following section, however one pertinent observation shown in Figure 6b is that collected particulate volumes during the period in which 8 nm particles are being monitored were an order of magnitude smaller than for the 13 nm particles. Following this period in which 8 nm diameter particles were measured and continuing for the remainder of the measurement period, the volume fraction for 13 nm diameter particles remained below 1. A slight increase in ammonium and an increase in the collected particulate volume can be seen during the period 10:00–11:00. This is associated with a regional growth event of 20–30 nm diameter particles as shown on Figure 6b. During these series of events the Nano TDMA monitored the volatility of 4 nm diameter particles, yet there were insufficient particle counts to provide a statistically significant result.

Figure 7 shows the measurement period spanning 8:00 to 16:00 on 26 August 2002, characterized by two plume impact events occurring at 10:25 and 14:05. During
this measurement period we left the TDCIMS analysis diameter fixed at 8 nm to observe relative concentration changes for particles of this size. At these low ambient concentrations and with the instrument measuring particles in the 8 nm size class, the TDCIMS signal is weak. This is clearly seen in the plot of collected particulate volume (Figure 7b), with values ranging from \((0.001–0.006) \times 10^{-18}\) m\(^3\), or 2 orders of magnitude smaller than that recorded for 13 nm particles on 22 August. Because of the limited amount of sample used for analysis, the data for this period show greater uncertainties and large scatter. In spite of this, the TDCIMS data show increases in the ammonium volume fraction that follow the two events by 1 hour and 40 min, respectively (see Figure 7c and Table 2). The large values for the volume fraction during the events (14.9 ± 5.6 and 16.0 ± 6.0) suggest much higher concentrations of ammonium than that observed in an equal volume of pure ammonium sulfate particles, a point which will be discussed next. Nano TDMA measurements were not made during this period.

6. Discussion

[29] The TDCIMS measurements of ammonium performed on 22 and 26 August 2002 (Figures 6c and 7c) are characterized by volume ratios significantly greater than 1, meaning there is more ammonium in the particle than can be explained by a model of pure ammonium sulfate. This was observed on occasion in earlier studies of sub-20 nm ambient aerosol in Boulder, Colorado [Smith et al., 2004], and may be caused by a variety of reasons:

[30] 1. While we have made our best effort to reduce uncertainties in those values required to derive the collected particulate volume, it is undeniably difficult to measure particles in the 6–10 nm diameter range. It is therefore

**Figure 5.** Time series plots of (a) particle size distributions, (b) TDCIMS collected particulate volume, and (c) ammonium volume fractions directly following a new particle formation event on 17 August 2002. Horizontal bars on each point in Figures 5b and 5c show TDCIMS collection period. Vertical dashed lines show time span for new particle formation event.
likely that there may be systematic biases in the values for \( n(D_p) \) as well as the efficiency factors in equations (6a) and (6b).

[31] It also cannot be ruled out that there may have been a small change in operating parameters that was more strongly reflected in the analysis of the 8 nm size class. Recent laboratory studies have shown that the TDCIMS may have a size-dependent chemical response to slight changes in operating parameters such as filament position during collection and/or analysis. The very low collected particulate volumes associated with the 8 nm measurements support both possible scenarios.

[32] We will continue to investigate these effects. However, the observation that the increases in ammonium volume fraction are closely correlated with new particle formation events is clear.

[33] The measurements of the chemical composition of newly formed particles shown in Figures 3–7, as well as those performed on other days and presented in Table 2, can be summarized as follows. Prior to a new particle plume impact or regional growth event, the concentration of ammonium and sulfate in 6–15 nm diameter particles is lower than that which would be expected for pure ammonium sulfate particles, with average ammonium and sulfate volume fractions in the range of 0.12–0.55. The exception to this appears to be the measurements of 8 nm particles on 26 August, although as discussed above these measurements are probably biased by systematic errors related to the estimation of collected particulate volume. A new particle formation event was always followed by an increase in the volume fractions of these compounds, usually to values of close to 1. These peaks were delayed in time from the start of the actual events, sometimes by as much as 2 hours as in the case of 17 August. There are many possible reasons for this delay. It is likely due to the fact that, in order for the TDCIMS instrument to be able to collect sufficient mass for

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**Figure 6.** Time series plots of (a) particle size distributions, (b) TDCIMS collected particulate volume, and (c) ammonium volume fractions directly following new particle formation events on 22 August 2002. Note that plotted particulate volumes for 8 nm particles in Figure 6b are multiplied by 10 to improve readability. Horizontal bars on each point in Figures 6b and 6c show TDCIMS collection period. Vertical dashed lines show time span for new particle formation event.
analysis, particles need to grow larger than the sub-10 nm sizes that characterize the start of a nucleation burst. Furthermore, the TDCIMS is especially sensitive to larger particles within the size class since its measurement is based on particle mass. Finally, meteorology may play a role in determining when particles from the plume that have grown to sufficient size actually reach the point of measurement. This latter effect may explain the variability in the delay.

After reaching its peak, the sulfate volume fraction in 13 nm diameter particles returned to values smaller than 1 without a significant increase in collected particulate volume. This suggests that one or a combination of the following may be occurring: (1) a sulfur acid-enriched air mass passed by the sampling site, which led to the new particle formation, and (2) ambient surface area decreased during these periods, which lead to a sudden decrease in condensational loss and an increase in new particle formation. The return to volume fractions smaller than one suggests that the conditions that lead to new particle formation were limited in their time span, and returned to background conditions after the event. A detailed study of these effects is presented in the companion paper by McMurry et al. [2005]. The observations of ammonium following nucleation events showed the same general trends as sulfate. In some cases higher concentrations of ammonium were observed in 8 nm diameter particles compared to 13 nm diameter particles. One event did not show this trend (17 August 2002), however, in no instances was it observed that 13 nm diameter particles had higher concentrations of ammonium compared to the smaller particles. Again, one possible contribution to this observation would be errors associated with the estimation of collected particulate volume, as discussed above.

The Nano TDMA results add support to the argument that particles formed from nucleation events during ANARChE are composed of ammonium and sulfate. This is presented in detail in a companion paper [Sakurai et al., 2005], but briefly summarized here. During the periods that
the TDCIMS measured enriched sulfate in nanoparticles following nucleation on 23 and 25 August 2002, the Nano TDMA measurements made on these days concluded that these were hygroscopic and nonvolatile, respectively. This is consistent with the Nano TDMA response to pure ammonium sulfate nanoparticles. During the three measurement periods in which ammonium was quantified, the Nano TDMA was successful in making measurements on only one day. On that day (17 August 2002) Nano TDMA measurements of 8 nm diameter particle volatility found that these particles decreased in diameter by 4 nm when exposed to 150°C, which is again in agreement with laboratory studies of pure 8 nm diameter ammonium sulfate particles.

[16] In another companion paper in this issue, Stolzenburg et al. [2005] studied regional growth events in order to compare the measured modal growth rates with calculated rates that account for condensation, intramodal coagulation of nucleation mode particles, and extramodal coagulation of nucleation mode particles with preexisting particles. When condensation was modeled as the diffusion of sulfuric acid molecules to the particle surface (the rate limiting step) followed immediately by neutralization by excess ammonia, good agreement was found with the observed growth rates. If neutralization from ammonium were not included in the model, the result would have been a general underprediction of growth rates. Thus this study of the observed particle growth rates supports our conclusion that ammonium and sulfate were major constituents in these particles. Another conclusion from the Stolzenburg et al. study is that, often, larger diameter growth events are not adequately described by sulfate alone. This is supported by our observations from 23 August (Figure 3), where we suggest that nonsulfate compounds may be partially responsible for this larger diameter regional growth event.

[37] A significant result of the current study is the observation that ammonium and sulfate are the only measurable ions for particles in the 6–15 nm diameter range. The fact that the measured volume fractions were often smaller than 1 means that these particles were composed of other compounds that could not be identified with the TDCIMS in the configuration used during ANARChE. Earlier measurements of sub-20 nm ambient aerosol in Boulder, Colorado, show that the instrument is capable of detecting a variety of compounds. Those measurements were made of particles that comprised the low-diameter end of the accumulation mode. In that study nitrate was found to be a major constituent of particles [Smith et al., 2004], whereas in the current study no nitrate was detected. In addition, as stated earlier, we have performed laboratory calibration tests with numerous organic compounds, including dimethylamine, pinic acid, pinonaldehyde. None of these compounds were observed in the particles. Finally we monitored the ethyl cation (29 Th), a commonly observed fragment ion from the thermal decomposition of larger organic compounds, and again did not observe this ion in the 6–15 nm diameter particles during the study.

[38] The results of this study, although unique to the Atlanta area, are similar to those observed in the Pittsburgh study as reported by Zhang et al. [2004]. In that study, as in ours, newly formed particles appear to be primarily sulfate. In the Pittsburgh study these 18–33 nm diameter particles are neutralized by ammonium 10–40 min after they are first observed. On the basis of those observations the authors hypothesized that particles are more acidic during the initial stages of growth following nucleation. Our measurements of 6–15 nm diameter particles reported here show that levels of both ammonium and sulfate start to increase 30 min to 2 hours following the observation of new particle formation. We attribute this to the time required for particles to grow large enough for analysis since both signals appear to be delayed by a similar amount, however, since we cannot measure positive and negative ions concurrently one cannot unequivocally rule out the possibility that the nascent particles are acidic as hypothesized by Zhang et al.

7. Conclusion

[39] We have reported the first measurements of the chemical composition of size-segregated 6–15 nm diameter atmospheric aerosol. These measurements were made following new particle formation events in Atlanta, Georgia, over the period 13–30 August 2002 during the Aerosol Nucleation and Real-time Characterization Experiment (ANARChE) using the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS). Concurrent measurements by a Tandem Differential Mobility Analyzer (Nano TDMA) as well as measurements of particle growth rates and gas condensate concentrations support the conclusion that ammonium and sulfate are essential components of these newly formed particles. No other compounds were identified in the particles in this size range.

[40] Additional measurements are planned in order to confirm the results of this study and to assess the importance of other compounds in the processes of nucleation and growth. These sites will include a one that is influenced both by local anthropogenic emissions and biogenic emissions from nearby conifer forests (Marshall, Colorado), and one located NE of Mexico City (part of the MIRAGE-Mexico field campaign planned for March 2006). Further improvements are being made to the TDCIMS instrument, including a temperature programmed thermal desorption capability in which the collection filament can be slowly heated from room temperature to ca. 300°C. This should facilitate the study of organics in the particles by minimizing fragmentation of the parent ions produced following desorption.

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