Evaporation of Ammonium Nitrate Aerosol in a Heated Nephelometer: Implications for Field Measurements

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Ammonium nitrate is a semivolatile aerosol component under typical ambient conditions and thus difficult to measure. In the field, the aerosol scattering coefficient is usually measured with a nephelometer by heating the ambient aerosol to a low reference relative humidity (∼40%) in order to measure a light scattering coefficient that is intrinsic to an aerosol rather than dependent on atmospheric relative humidity. In this paper, we examine the decrease in the light scattering coefficient of ammonium nitrate aerosol due to evaporation in a heated nephelometer. Changes in the scattering coefficient of a laboratory-generated ammonium nitrate aerosol are measured as a function of mean residence time and temperature within the nephelometer sample volume. At the same time, the change in the aerosol size distribution due to ammonium nitrate evaporation is directly measured with a laser particle counter. The change in the aerosol size distribution and scattering coefficient is modeled as a function of mean residence time and temperature. Model results for the change in the aerosol scattering coefficient due to evaporation agree with measurements to within 10%. Application of the theory to conditions typical of NOAA field sites suggests that the decrease in the aerosol scattering coefficient due to the evaporation of ammonium nitrate is generally less than 20%.

Introduction

The aerosol light scattering coefficient, typically measured by an integrating nephelometer (1, 2), is a key aerosol property affecting atmospheric visibility as well as the extent to which aerosols scatter shortwave radiation away from the earth's surface, termed direct shortwave aerosol radiative forcing (3). Aerosols often contain hygroscopic inorganic salts (i.e., ammonium sulfate, ammonium nitrate) which increase in size with increasing relative humidity (RH), resulting in an increase in the aerosol light scattering coefficient (4). In order to measure a light scattering coefficient that is intrinsic to an aerosol rather than dependent on atmospheric relative humidity, it is customary to perform measurements at a relatively low RH (typically less than 40%). This is commonly accomplished by heating the ambient airstream under the assumption that aerosol chemical species other than water are not volatilized. The evaporation of relatively volatile aerosol chemical species, such as ammonium nitrate, becomes a concern in sampling systems that heat ambient air.

Ammonium nitrate aerosol is common to urban areas and in some cases contributes substantially to the total aerosol extinction on a regional scale. In Los Angeles, a significant fraction of the aerosol mass in the accumulation mode (i.e., having diameters between 0.1 μm and 1.0 μm) has been attributed to particulate ammonium nitrate (5, 6). Similarly, it has been reported that ammonium nitrate can account for roughly 20% of the total aerosol extinction measured during the winter in Denver (7). Measurements in The Netherlands have estimated that light scattering by nitrate aerosol is comparable to that of sulfate in the summer and even greater during the winter (8). Although measurements indicate ammonium nitrate is prevalent in urban plumes, there is a great deal of uncertainty associated with measurement of the aerosol mass size distribution because of the volatile nature of this aerosol (9, 10).

The NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) maintains a series of regional and baseline monitoring stations to address issues related to aerosols and climate change. Measurements include the total aerosol number concentration, total light scattering and backscattering coefficients, light absorption coefficient, ionic composition, and total aerosol mass (11). Stations impacted significantly by urban plumes are Bondville, IL, Sable Island, Nova Scotia, and Niwot Ridge, CO. At NOAA aerosol monitoring stations, the inlet airstream is heated to maintain a reference RH of 40% (11). When the ambient RH is less than 40%, no heating takes place at the inlet. The heating generally results in a several degrees kelvin increase in the air stream temperature, with a maximum value of 314 K. In addition, the integrating nephelometer used to measure the aerosol scattering coefficients heats the airstream by several degrees kelvin. Therefore, the possibility arises of evaporating a volatile aerosol chemical species, such as ammonium nitrate, resulting in a decrease in the aerosol scattering coefficient. The extent of such evaporation and the resultant decrease in the aerosol scattering coefficient depend on several factors including the residence time of air in the heated region, the temperature, the relative humidity, and the initial particle size distribution.

The evaporation of ammonium nitrate has been investigated under a variety of laboratory and field conditions. Larson and Taylor (12) studied the evaporation of ammonium nitrate aerosol solution droplets (RH ∼60%, T ∼290 K) by measuring the change in the aerosol size distribution as a function of residence time in a diffusion stripper designed to remove HNO3 and NH3. The observed changes were in agreement with theoretical predictions based on gas phase diffusion and vapor pressures calculated for pertinent solution chemical compositions. Harrison et al. (13) measured aerosol size distributions using an impactor downstream of a denuder designed to scrub NH3 and HNO3 from the airstream. In contrast to the results of Larson and Taylor, evaporation of ammonium nitrate was found to be much slower than predicted by theory, suggesting the existence of an unknown kinetic constraint inhibiting mass transport from aerosol particles. Richardson and Hightower (14) levitated anhydrous ammonium nitrate crystalline solid and supersaturated liquid particles in an electrode transport balance at room temperature and measured changes in the particle radius with time. Their measurements agreed with theoretical predictions based on thermodynamic properties and kinetic theory for evaporation of particles in a vacuum, under the assumption that the mass proportional to the particle mass.
accommodation coefficient was initially 0.02, decreasing to 0.004 after 4 h. Indeed, recent modeling results have indicated that there are several factors that must be considered when estimating the evaporation of ammonium nitrate based on lab conditions including the aerosol size distribution, and use of an appropriate evaporation theory. In addition to laboratory studies, field studies have indicated that the volatilization of ammonium nitrate aerosol may be significant for filters and impactors under some atmospheric conditions.

The focus of this paper is to study the effect of ammonium nitrate aerosol evaporation in a heated nephelometer on the aerosol light scattering coefficient under conditions representative of field sampling conditions. We focus on measurement and modeling of the evaporation of ammonium nitrate aerosol at a low relative humidity (~10%, in order to dry the aerosol) as a function of temperature (300–320 K), nephelometer mean residence time, and initial aerosol particle size distribution. We predict the decrease in the aerosol light scattering coefficient expected for a variety of field sampling conditions.

Experimental Approach

Figure 1 shows the experimental setup used to measure the evaporation of ammonium nitrate aerosols within an integrating nephelometer as a function of temperature and residence time. An atomizer generated a polydisperse ammonium nitrate aerosol that was dried and passed through a TSI Model 3071 differential mobility analyzer (DMA). The flow settings of the DMA were 2.0 L min\(^{-1}\) for the sample flow and 7.5 L min\(^{-1}\) for the sheath flow which allowed for the generation of a narrow aerosol size distribution having singlet particles (particles of one elementary unit of charge) of 0.40 \(\mu\)m diameter. After passing through the DMA, the aerosol stream was mixed with a dry airstream that had been scrubbed to remove NH\(_3\) and HNO\(_3\) (with packed columns of citric acid and sodium bicarbonate), and filtered to remove aerosol particles. The temperature and RH of the airstream were measured directly upstream and downstream of the nephelometer using Vaisala Model 50Y temperature and relative humidity sensors. The aerosol then passed through a TSI 3563 three-wavelength integrating nephelometer that measured the aerosol scattering and backscattering coefficients at 450, 550, and 700 nm (with the aerosol scattering coefficient at 450 nm being reported in this paper). The nephelometer was maintained at a constant temperature by a process controller that supplied power to heating tape wrapped around the outside of the nephelometer control volume. After passing through the nephelometer, the aerosol was diluted with clean air in order to ensure a flow rate of 27 L min\(^{-1}\) through a Climet 6300 Laser Particle Counter (LPC), which measured the diameters of particles greater than 0.3 \(\mu\)m. The LPC was calibrated with known size ammonium sulfate aerosol particles generated with the DMA. In addition, the total aerosol number concentration of particles greater than 0.01 \(\mu\)m in diameter was measured with a TSI 3760 Condensation Nucleus Counter (CNC) at the exit of the nephelometer.

Experiments were performed at temperatures from 300 K to 320 K in increments of 5 K. At each temperature, the nephelometer flow rate was maintained at 5 L min\(^{-1}\), 10 L min\(^{-1}\), and 18 L min\(^{-1}\) which corresponds to mean residence times of 26 s, 13 s, and 7.3 s, respectively. At each temperature and flow rate, the scattering coefficients (\(\sigma_{\text{sp}}\)) were measured, as well as the concentrations of particles greater...
than 0.01 μm in diameter (CNC) and the size distribution of particles greater than 0.3 μm in diameter (LPC).

To examine whether the nephelometer is well mixed (i.e., a completely stirred reactor), a polydisperse ammonium sulfate aerosol was generated with an atomizer and mixed with clean, dry air. The number concentration was measured directly downstream of the nephelometer with a CNC, using an experimental setup similar to Figure 1, but without the DMA. At each flow rate, filtered air from a HEPA capsule filter internal to the nephelometer was switched into the airstream in order to flush aerosol particles from the control volume, and the number concentration of particles at the outlet was recorded as a function of time. The experiment was conducted at three flow rates. Figure 2 shows the decay of the normalized particle number concentration (particle concentration at a given time, \(N_t\), divided by the initial concentration, \(N_i\)) with time. Also shown are the theoretical curves for the change in the particle concentration with time, assuming the nephelometer is well mixed (with a sample volume of 2.49 L). The theoretical curves are in general agreement with the measurements, confirming that for the flow rates used in this study the nephelometer can be modeled as a well-mixed system.

In addition to testing the nephelometer mixing assumptions, possible temperature-dependent loss of particles to the nephelometer walls was determined as a function of residence time using nonvolatile ammonium sulfate aerosol with the same input aerosol size distribution as that used for the ammonium nitrate experiments. Results showed that for a nonvolatile aerosol the size distribution was similar both upstream and downstream of the nephelometer and was unaffected as the nephelometer temperature was increased, demonstrating that wall losses were negligible up to at least 320 K. In addition, the aerosol scattering coefficients varied by less than 5% at each temperature because the total aerosol number concentrations and size distributions remained relatively constant.

**Modeling the Effect of Particle Evaporation on the Light Scattering Coefficient.** The ratio of the scattering coefficient of an aerosol in a nephelometer for a given temperature, \(T\), wavelength, \(\lambda\), and residence time, \(r\), to that of the initial aerosol scattering coefficient (i.e., scattering coefficient of the aerosol size distribution at the nephelometer inlet) is denoted

\[
R_T(r) = \frac{\alpha_T(r)}{\alpha_T(0)}
\]

where \(\alpha_T(0)\) is the aerosol scattering coefficient at a given \(T\), and \(\alpha_T\) is the scattering coefficient of the aerosol size distribution at the nephelometer inlet. From the measured size distribution, the initial aerosol scattering coefficient can be estimated as

\[
\alpha_T(0) = \frac{2}{4} \sum_{j=1}^{m} D^2_{pj} K_{p j} n_{Tj}(0)
\]

For our calculations, the size distributions are divided into 17 size bins \((m = 17)\) having midpoint diameters ranging from 0.30 μm to 0.64 μm in increments of 0.02 μm. The aerosol scattering efficiency, \(K_{p j}\), is estimated using the approach of Bohren and Huffman (16) under the assumption that the particles are spherical and have a refractive index of 1.47 (14), and \(n_{Tj}(0)\) is the number concentration of aerosol particles in the bin centered at \(D_{pj}\) at a given temperature for the initial particle size distribution.

The estimation of \(\alpha_T(r)\) for a size distribution of particles within the nephelometer (i.e., for \(r > 0\)) is considerably more complicated than for \(\alpha_T(0)\) since the aerosol size distribution that initially enters the nephelometer is heated to a temperature, \(T\), which causes the particles to decrease in size due to evaporation. \(\alpha_T(r)\) can be written as

\[
\alpha_T(r) = \frac{2}{4} \sum_{j=1}^{m} \sum_{k=1}^{N} D^2_{pj} K_{p j} n_{Tj,k}(r)
\]

where each value of \(D_{pj}\) is divided into \(N\) intervals of particle residence time ranging from 0.1 to 100 s. In order to estimate \(n_{Tj,k}(r)\), we assume that the nephelometer control volume is well mixed, as previously discussed, and that particles within the nephelometer of initial diameter \(D_{pj}\) have a residence time distribution that is exponentially weighted based on the mean residence time within the nephelometer. Therefore, the particle number size distribution in the nephelometer is the sum of the exponentially weighted size distributions having initial diameters \(D_{pj}\). In order to estimate \(n_{Tj,k}(r)\), it is necessary to estimate the change in size of each initial particle size at a given temperature due to evaporation. The change in diameter due to evaporation in the nephelometer at a given temperature can be solved based on the approach of Fuchs and Sutugin (17) as follows:

\[
\frac{dD}{dt} = \left(\frac{M_{NH_4NO_3}}{\rho_{NH_4NO_3} A T}\right) F(K)AD_{p}^{1/2} K_{p}^{1/2} D_{p}^{1/2}
\]

where \(M_{NH_4NO_3}\) and \(\rho_{NH_4NO_3}\) are the molecular weight and density of ammonium nitrate, \(D\) is the root mean square diffusivity of ammonia and nitrate away from the particle surface as discussed by Weidler and Seinfeld (18), \(F(K)\) is a correction for free molecular effects as described by Pandis and Pilinis (19), \(A\) is a correction for interfacial mass transport limitations (in this case, equal to 1 since we assume a mass accommodation coefficient of 1 (15)), and \(K_{p}\) is the vapor pressure product of ammonia and nitric acid directly above the particle surface (20). For dry ammonium nitrate, there is a more than 20-fold rise in \(K_{p}\) from 300 to 320 K, demonstrating the sensitivity of the change in particle diameter with time to temperature (20). It should be noted that above the deliquescence point (RH = 63% for typical ambient conditions) the value of \(K_{p}\) depends on the RH as well as the temperature. As the RH increases, \(K_{p}\) decreases, and the rate of evaporation of ammonium nitrate from the particle slows.

The experiments were conducted at RH values between roughly 5% and 15%; we therefore assume that the particles are dry with no associated water. The possibility cannot be excluded that the particles are supersaturated with respect to aqueous ammonium nitrate, and exist in a metastable state as concentrated ammonium nitrate droplets. This would result in greater solute vapor pressures over the particles and hence increased evaporation rates compared to the dry aerosol (21).

To estimate \(n_{Tj,k}(r)\) for an initial size distribution, we first use eq 4 to predict the change in particle diameter for each
diameters, determine the size distributions of particles having initial estimates of the change in diameter with time (eq 4) to the residence time distribution functions are combined with distributions for mean residence times of 7.3, 13.0, and 26.0 s. Figure 3 shows the modeled and measured number size distributions at 300 K and 320 K for (a) \( \tau = 7.3 \) s, (b) \( \tau = 13.0 \) s, and (c) \( \tau = 26.0 \) s.

The results show that the theoretical model employed here accurately describes the decrease in the aerosol scattering coefficient as a function of aerosol physical properties, nephelometer temperatures, and residence times and therefore can be used to predict the decrease in the aerosol scattering coefficient of ammonium nitrate under field measurement conditions. Here we estimate the ratio of the scattering coefficient at \( T \) and \( r \) to the initial aerosol scattering coefficient, \( R_{\tau}(t) \), for a range of possible field conditions and discuss the decrease in the scattering coefficient expected for the NOAA aerosol sampling protocols.

Figure 5 shows the inlet configuration for a typical NOAA aerosol monitoring station. The aerosols are drawn into a main stack at a flow rate of 1000 L min\(^{-1}\), which corresponds to a mean residence time in the stack of roughly 7 s. Within the stack, the temperature and RH remain at ambient conditions. The aerosol then enters a section that is heated in order to achieve an RH of 40%. Depending on the ambient temperature and RH, the airstream can be heated up to 314 K (which is an upper limit set point value at the NOAA monitoring stations). The heated air then enters a nephelometer for a time probability of finding a particle that has been in the stack at a flow rate of 1000 L min\(^{-1}\), which corresponds to a mean residence time in the stack of roughly 7 s. Within the stack, the temperature and RH remain at ambient conditions. The aerosol then enters a section that is heated in order to achieve an RH of 40%. Depending on the ambient temperature and RH, the airstream can be heated up to 314 K (which is an upper limit set point value at the NOAA monitoring stations). The heated air then enters a nephelometer.
eter which measures the aerosol scattering and backscattering coefficients at 450, 550, and 700 nm. The nephelometer lamp heats the airstream by an additional 2–5 K. At the Bondville station, the mean temperature within the nephelometer over an entire year (based on hourly averages) is 301 K, with temperatures exceeding 310 K 5% of the time and temperatures above 320 K roughly 1% of the time. For the flow rates employed, the mean residence times in the heated section of the inlet and the nephelometer are 2 s and 4.8 s, respectively. Because the residence time and temperature in the nephelometer are greater than in the heated section of the inlet, we assume that the evaporation of particles in the heated inlet section is negligible compared to that in the nephelometer.

In order to estimate the decrease in the aerosol scattering coefficient of ammonium nitrate for specific field conditions, it is necessary to measure the initial particle size distribution of the ambient aerosol. Because of evaporation, as discussed previously it is difficult to measure the ammonium nitrate aerosol size distributions by traditional methods such as impactors (9, 10). Therefore, there is not a great deal of information on the size distributions of ammonium nitrate reported in the literature. More importantly, there is little information available on the contribution of ammonium nitrate aerosol to the total aerosol extinction, with the exception of a study in Denver (7), and several studies in The Netherlands (8, 22). John et al. (6) measured the mass size distributions of ammonium nitrate aerosol in Los Angeles and report data in terms of lognormal moments. Based on these measurements, we assume a similar lognormal ambient size distribution at the NOAA sampling sites having a geometric number median diameter \( D_{p,g} \) of 0.4 \( \mu m \) and a GSD of 1.6.

Model estimates of the decrease in the aerosol scattering coefficient at 450 nm for a given temperature with increasing mean residence time, \( \tau \), are shown in Figure 6. For a given mean residence time, the ratio of the final to initial scattering coefficient, \( R_T(\tau) \), decreases with increasing temperature, reflecting the \( K_{p}^{1/2} \) dependence on temperature. As indicated in the figure, for a mean residence time of 4.8 s typical of NOAA sites, the scattering coefficient decreases by at most 20% at 320 K. Again we stress that the estimated \( R_T(\tau) \) values are intended to be upper estimates of the change in the aerosol scattering coefficient due to evaporation, because of the assumption that the aerosol is composed entirely of ammonium nitrate and the assumption of maximum aerosol evaporation rate. There are several reasons that ammonium nitrate aerosols may take longer to evaporate in the atmosphere including the existence of ammonium nitrate solution droplets at RH values above the deliquescence point which result in lower \( NH_3 \) and \( HNO_3 \) vapor pressures above the particle surfaces, as well as organic surface coatings which inhibit gas phase transport (18).

![FIGURE 4. \( \sigma(\tau)/\sigma_{300}(\tau) \) measured and theory vs temperature for ammonium nitrate particles at (a) \( \tau = 7.3 \) s, (b) \( \tau = 13.0 \) s, and (c) \( \tau = 26.0 \) s.](image)

![FIGURE 5. Typical NOAA CMDL aerosol inlet design.](image)

![FIGURE 6. Ratio of scattering coefficient at \( T \) and \( \tau \) to initial scattering coefficient, \( R_T(\tau) \), vs mean residence time (\( \tau \)) for ammonium nitrate size distributions having a geometric number median diameter \( (D_{p,g}) \) of 0.4 \( \mu m \) and a geometric standard deviation (GSD) of 1.6.](image)
seen at a temperature of 320 K for which temperature, ranging from 300 to 320 K. As seen in the figure, for a given
figure, on the decrease in the aerosol scattering coefficient. In the
nitrate aerosol is roughly 40%. However, based on the few
scattering coefficient due to the evaporation of ammonium

![FIGURE 7. \( R_\tau(T) \) vs \( D_{p,g} \) for an ammonium nitrate aerosol with a GSD = 1.6 and \( \tau = 4.8 \) s.](image)

![FIGURE 8. \( R_\tau(T) \) vs \( T \) for an ammonium nitrate aerosol with \( D_{p,g} = 0.4 \mu m \), \( \tau = 4.8 \) s, and GSD's ranging from 1.0 (monodisperse) to 2.0.](image)

Figure 7 shows the effect of particle size and temperature on the decrease in the aerosol scattering coefficient. In the figure, \( R_\tau(T) \) is plotted vs geometric number median diameter, \( D_{p,g} \), for a geometric standard deviation of 1.6, for temperatures ranging from 300 to 320 K. As seen in the figure, for a given temperature, \( R_\tau(T) \) decreases as \( D_{p,g} \) decreases. This is due to the inverse dependence on diameter of the rate of diameter change due to evaporation, as shown in eq 4. Figure 7 suggests that the maximum decrease in the scattering due to evaporation of ammonium nitrate aerosol during field sampling is 40% (for \( D_{p,g} = 0.2 \mu m \) and \( T = 320 \) K), although as noted above it is difficult to verify that this is a realistic value for \( D_{p,g} \) for the conditions at the aerosol monitoring stations. Figure 8 shows the effect of GSD on \( R_\tau(T) \) for a mean residence time of 4.8 s and an assumed ammonium nitrate particle number mean diameter of 0.4 \( \mu m \). The effect of GSD is clearly seen at a temperature of 320 K for which \( R_\tau(T) \) increases from 0.58 for a monodisperse aerosol of 0.4 \( \mu m \) to 0.90 for a GSD = 2.0. This increase is due to the increase in the number of particles having diameters greater than \( D_{p,g} \) as the GSD increases. As shown in eq 2, the scattering coefficient is a function of \( D_p^2 \) as well as \( K_o \). As the GSD increases, the relative number of particles greater than \( D_{p,g} \) increases as does \( K_o \) for these particles, which results in an increase in the scattering coefficient as well as \( R_\tau(T) \).

In summary, the model estimations of \( R_\tau(T) \) suggest that for a worst-case scenario at NOAA field sampling locations (i.e., \( T = 320 \) K, \( D_{p,g} = 0.2 \mu m \)) the decrease in the aerosol scattering coefficient due to the evaporation of ammonium nitrate aerosol is roughly 40%. However, based on the few aerosol size distribution measurements available, the decrease in the aerosol scattering coefficient is generally expected to be less than 20%.

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**Literature Cited**


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