

Growth and Structural Change of Combustion Aerosols at High Relative Humidity

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Condensational growth and structural changes of combustion aerosol particles were investigated by means of a tandem differential mobility analyzer. Sodium chloride particles, carbon particles, and freshly emitted combustion particles with diameters between 50 and 100 nm were investigated. A dry, highly monodisperse aerosol was exposed to high relative humidity (RH), and the electrical mobility diameter was measured as a function of RH. A growth factor was determined by comparing the dry particle mobility diameter with the diameter of the humidified particles. NaCl particles showed the expected behavior with a rapid increase of the growth factor at the deliquescence humidity. Carbon particles shrank to about 85% of their original diameter when exposed to RH = 90%. This shrinking was attributed to capillary condensation in small angle cavities of aggregates. Capillary forces induced on any asymmetric part of the particles cause them to become a more compact structure. Particles emitted from a four-stroke spark ignition engine showed a different behavior: Smaller particles (dry diameter $d_0 = 51.5$ nm) did not change in size up to RH = 95% and then started to grow. Larger aggregates ($d_0 = 108$ nm) first shrank to approximately 99% of their original size and then started to grow at RH $\geq 95\%$. That means that the combustion particles were at least partly covered with material able to reduce the water pressure at the particle surface. In addition, these particles were more compact compared to carbon particles, resulting in less restructuring. With increasing aging time in a dark bag, the growth factor of the combustion particles increased.

Introduction

Ambient aerosols contain hydrophobic and hydrophilic material. The amount of these components will determine

the response of the particles to a change in relative humidity (RH). The water uptake of an aerosol particle from the gas phase will change its physical and chemical properties including its light absorption and scattering characteristic. On the other hand, the water layer can absorb other species from the surrounding air, e.g., nitric oxides.

Hydrophobic material is not easily incorporated into water droplets and may stay suspended in the air for a long time. This allows soot to be transported over large distances before being removed from the atmosphere. According to the Köhler model, the growth of spherical particles due to water vapor condensation depends on the chemical composition and on the initial diameter of the particles as well as on the RH of the ambient air (1). Thus the amount of water-soluble material on insoluble particles is very important for the life cycle of aerosol particles.

Soot particles are usually considered to be hydrophobic. However, field experiments in populated areas have indeed shown that when an ambient aerosol is subjected to an RH of 85% often two modes result, i.e., a more hygroscopic and a less hygroscopic mode (2-4). Svenningsson et al. (2) showed under certain conditions that the less hygroscopic fraction may exhibit a certain growth (by a factor of about 1.1) at RH = 85%. McMurry and Stolzenburg (3) did not observe a significant growth for the less hygroscopic fraction.

The question arises if this is also the case for freshly emitted soot particles or if aging processes lead to a higher hygroscopicity. If the latter is true, it will be of interest which aging processes (e.g., chemical modification of the particle surface, coagulation leading to internal mixture) are mainly responsible for this fact. In this paper, we present hygroscopicity measurements of fresh soot particles from a spark ignition engine and also first results of aged particles.

Various authors investigated the hydration properties of combustion aerosols with a number of different methods. One approach used an electrodynamic balance. A DC voltage balances a charged particle ($d > 10$ μm) against gravity, and its mass can be followed as a function of time and gas composition. Andrews and Larson (5) showed with this technique that an originally hydrophobic carbon black particle will sorb significant amounts of water at RH $\leq 90\%$ when the particle is coated with an organic surfactant such as Tween 80 or azelaic acid.

Huang et al. (6) subjected diesel engine aggregates to several water condensation and evaporation cycles and observed a significant collapse of these particles. These measurements were performed by measuring the fractal dimension with an environmental scanning electron microscope on particles larger than 1 μm .

Vartiainen et al. (7) measured the water uptake of combustion aerosols by weighing filter samples while varying the RH in the weighing chamber. Significant water uptake was observed: Diesel soot samples increased their mass by about 2% as RH was increased from 40% to 90%. The observed mass increase was 3.5 times greater for gasoline soot samples and about 4 times greater for wood smoke compared to diesel soot.

The above approaches to measure the hygroscopicity of combustion aerosols suffer from different drawbacks. The electrodynamic balance works only for aerosol particles of

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the coarse particle mode (d = several microns) and therefore can not be applied for combustion particles which appear in the nucleation and accumulation mode. The same is also true for Huang et al. (6). Regarding the third approach, it is difficult to compare the hygroscopicity of filter samples with the hygroscopic behavior of an aerosol. Capillary condensation will be enhanced for particles collected on a filter compared to particles suspended in the air. Therefore, filtered material appears to be more hygroscopic than the particles themselves. Since our goal is the determination of the hygroscopicity of small aerosol particles, we decided to use a setup allowing an in-situ measurement as described below.

Experimental Section

Particle Generation. Three different kinds of particles were used.

(1) Sodium chloride (NaCl) particles generated by atomization of an aqueous solution in compressed air followed by a diffusion drier.

(2) Carbon particles produced by spark discharges between graphite electrodes (8). The carrier gas was either nitrogen or argon. These particles were highly agglomerated.

(3) Fresh combustion particles emitted from a four-stroke spark ignition engine (Yamaha EF600) operated at a load of 400 W. The engine was run with commercially available leaded fuel (lead content = 0.15 g/L), and it was placed in a chemical hood.

For the combustion aerosols, two kinds of sampling techniques were applied:

(a) Cold Dilution: With the ventilation of the hood, the exhaust gas was directly diluted (by a factor of about 7) and sampled at the top of the hood. The RH of the sample was $65 \pm 5\%$ at ambient temperature (23°C).

(b) Hot Dilution: Mixing of 1 part exhaust gas with 8 parts particle free air. This dilution air was heated up to exhaust gas temperature. In this case, the RH of the carrier gas was about 20% at ambient temperature.

Thus, the major difference between the two diluting techniques consisted of a different RH exposure of the aerosol before entering the tandem differential mobility analyzer (TDMA): In the first case, the particles experienced a much higher RH than in the second one. In both cases, typical number concentrations at the TDMA inlet were about 10^5 cm^{-3} .

Measurement of Particle Growth. The hygroscopicity of aerosol particles was studied by measuring the particle growth as a function of RH by a computer-controlled TDMA. Such a system was initially developed by Liu et al. (9) and improved by different researchers (2–4, 10–14).

The setup used in our case is shown in Figure 1. In all experiments, the aerosol was first dried in a silica gel diffusion drier and then fed into a coagulation chamber with a residence time of 2 min at a flow rate of 4 Lpm. Then, the particles were charged by a bipolar charger (^{85}Kr , 2 mCi), and a narrow size fraction was selected using a Hauke 100 MN differential mobility analyzer (DMA) operating with dry filtered sheath air with a flow rate of 40 Lpm, leading to a size resolution of $0.12 < \Delta d/d < 0.145$ for $50\text{ nm} < d < 110\text{ nm}$. The dry, highly monodisperse aerosol was humidified by passing it through a GORE-TEX tube surrounded by a thin water layer. The humidity was controlled by adjusting the temperature of this water layer. After electrostatic elimination of the particles, the humidity was

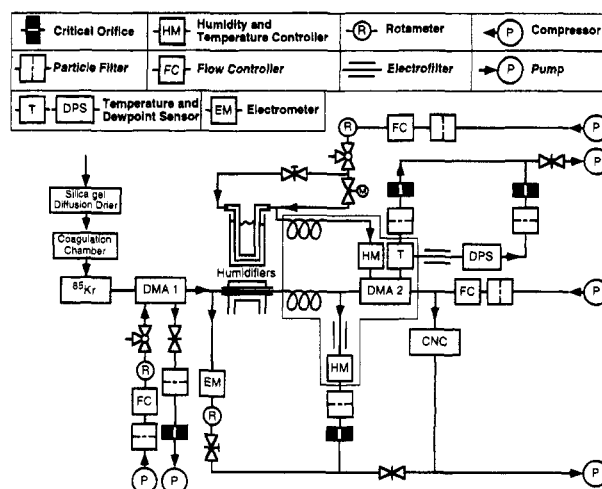


FIGURE 1. Experimental setup of the tandem differential mobility analyzer (TDMA).

measured with a capacitive humidity sensor (HP101A, Rotronic AG), and the particle concentration was monitored by an aerosol electrometer (i.e., a particle filter connected to an amperometer). After a residence time of 2.2 s in the humidifier, the new size distribution of the particles was determined with a second DMA (TSI 3071 replicate operating with 8 Lpm sheath air) connected to a condensation nuclei counter (CNC) (TSI 3760). Neither particle loss nor change in particle charge between the DMAs was observed. The sheath air was humidified in a similar way as the aerosol stream and controlled with a capacitive humidity sensor. The humidity of the excess air was measured with a dew point sensor (911 DEWALL, EG&G). The capacitive sensors were calibrated every second week with this dew point sensor. As the RH in the second DMA is most important for the final particle size, we used the data of the dew point sensor for the data evaluation. The temperature and the dew point of the excess air were measured with Pt100 electric resistances with accuracies of $\pm 0.1^\circ\text{C}$. Thus, RH was measured with a relative uncertainty of $\pm 1.5\%$ in the worst case.

The temperature of the humid air was monitored at three points, and great care was taken to have constant ambient temperatures in the whole system. To prevent a hysteresis effect in the particle growth, the RH of the aerosol was set 2% below the RH of the sheath air of the second DMA, assuming that the final growth to the equilibrium size took place in the "top region" of this DMA without affecting the size measurement. To get a high accuracy in the particle electrical mobility measurements, the excess air flows were kept constant by using critical orifices, and the sheath air flows were adjusted by mass flow controllers. During a measurement, the humidities before and inside the second DMA were kept on a constant level. The first DMA voltage was kept fixed while the second was scanned to evaluate the change of the particle diameter. A personal computer with analog-to-digital and digital-to-analog converters was used to control the temperatures and the humidity in the system as well as the DMA voltage settings. The CNC counts and the electrometer signal were also monitored.

Results and Discussion

Figure 2 shows typical size spectra for NaCl and carbon particles for two different relative humidities after the humidification, where all particles had a dry electrical

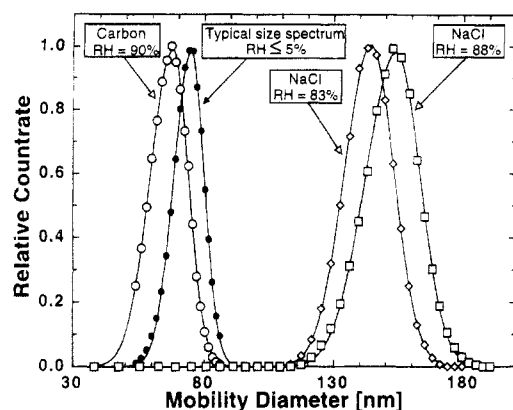


FIGURE 2. Typical size spectra for carbon particles (produced in N_2) and sodium chloride particles with dry diameters $d_0 = 73$ nm after exposure to different relative humidities.

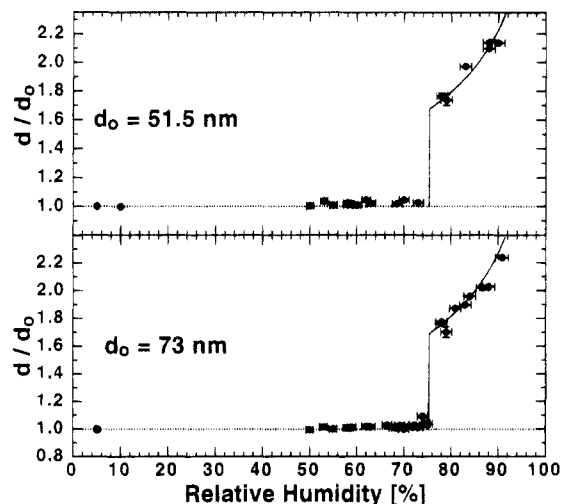


FIGURE 3. Growth factor d/d_0 vs. relative humidity for sodium chloride particles. The solid lines are theoretical curves, using the deliquescence humidity for particles with $d_0 \geq 100$ nm (15, 16).

mobility diameter of $d_0 = 73$ nm. The spectra were fitted using the Levenberg–Marquardt algorithm (15), and the mode diameters d_m (diameter with the highest count rate) were used to calculate the growth factors d/d_0 , defined as the ratio of the mobility diameter d of the humidified particles to the mobility diameter d_0 of the dry particles. The fitting procedure also calculated the confidence intervals for the fitted parameter d_m , assuming that the measured data points were normally distributed. In the figures, the uncertainties of diameter and RH are represented by vertical and horizontal error bars, respectively.

Figure 3 shows the measured growth factors of NaCl particles. Assuming that the electrical mobility diameter (measured with the TDMA) corresponds to the geometric diameter (used in the model), we find a good agreement between experimental and predicted theoretical data from Ferron and Soderholm (16) based on the Kelvin correction and Raoult's law. The observed deliquescence humidity at 20 °C gas temperature corresponds very well to the calculations of Tang and Munkelwitz (17), who reported a deliquescence humidity of 75.4% RH for NaCl particles with $d > 100$ nm.

Figure 4 shows measurements with carbon particles produced by spark discharges between graphite electrodes. The carrier gas was either nitrogen (purity: 99.999%) or argon (purity: 99.998%). With increasing RH, these particles shrank indicating a restructuration of the particles. This

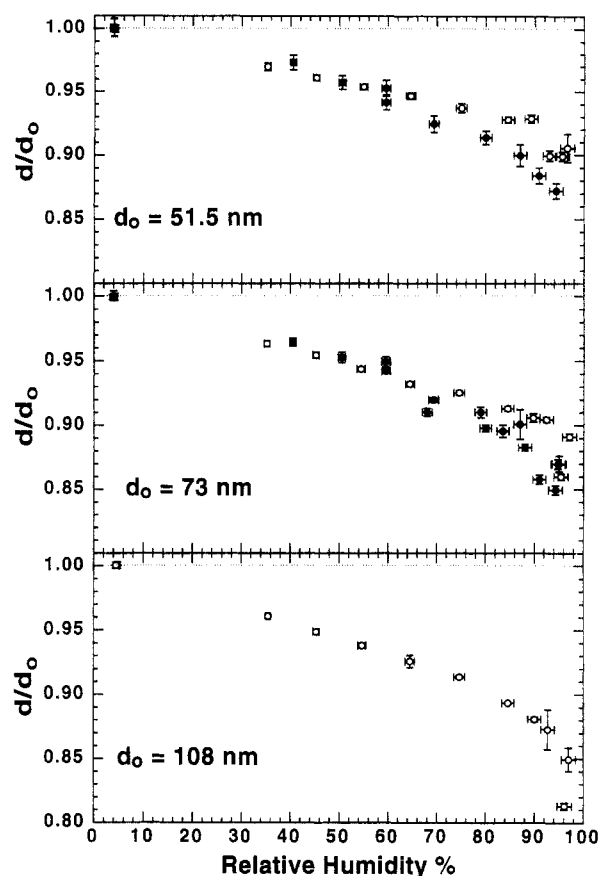


FIGURE 4. Growth factor d/d_0 vs. relative humidity for carbon particles produced in argon (○) or nitrogen (●). $d/d_0 < 1$ indicates a shrinking of the particles.

restructuration process was more pronounced for larger particles and for particles produced in nitrogen.

This fact can be explained as follows: the dry carbon particles are agglomerates having a nonspherical, fractal-like structure. Theoretical calculations by Crouzet and Marlow (18) illustrate that even at very low RH a region between two adhering spheres (radii > 10 nm) supports a pendular ring of condensation. This may result in a condensate–vapor interface with negative curvature. Therefore, the observed restructuration is most probably due to condensing water in small angle cavities of the aggregated particle. Condensed water leads to capillary forces on any asymmetric part of the aggregates, causing them to collapse. This can also be seen by fractal analysis of the carbon particles (produced in N_2) with a DMA combined with a low pressure impactor. This technique is described in detail by Schleicher et al. (19). The fractal dimension was found to be $d_f = 2.10$ for dry carbon particles and $d_f = 2.17$ for particles that were first humidified at 90% RH and then dried (20). This observation is in good agreement with the TDMA measurements. Based on the definition of the fractal dimension $m = cd^{d_f}$ (where m is the particle mass, d is the particle diameter in nm, and c is a constant) (21), one can derive a relation between the originally dry and the humidified aerosol:

$$\frac{d_{f, \text{hum}}}{d_{f, \text{dry}}} = \frac{\log(d_{\text{dry}})}{\log(d_{\text{hum}})} \quad (1)$$

We assume that the particle mass and the constant c do not change as a consequence of the humidification and drying cycle. If the fractal dimension of an aerosol increases

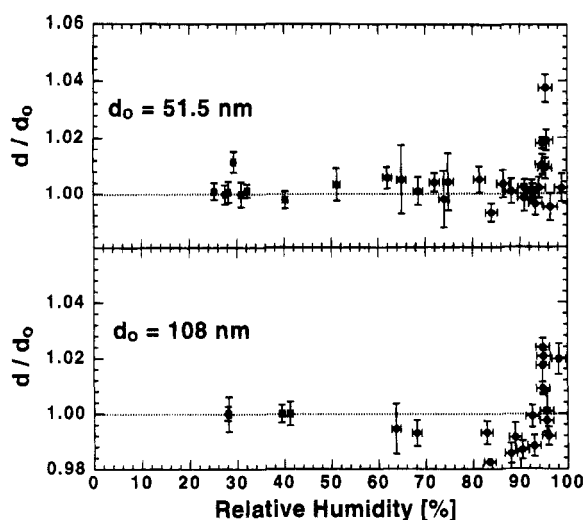


FIGURE 5. Growth factor d/d_0 vs relative humidity for fresh combustion particles.

from $d_f = 2.10$ to $d_f = 2.17$, this relation predicts a growth factor of 0.88 and 0.87 for $d_0 = 51.5$ nm and $d_0 = 73$ nm, respectively. This corresponds very well with the measurements made with the TDMA.

Particles produced in argon show a slightly smaller restructuring than particles produced in nitrogen. This different behavior might be explained by the presence of polar groups on the surface of the carbon particles produced in nitrogen. Such groups would enhance the wettability of the carbon surface. The difference in the chemistry of the particle surface with the two carrier gases is exemplified by photoelectron spectroscopy data: in nitrogen, the N 1s peak amounted to 19 atom % compared to 1.5 atom % with argon.

Such restructuring processes were demonstrated by other authors: Colbeck et al. (22) investigated aged smoke particles that were produced by combustion of liquefied petroleum gas. These particles were subjected to various high relative humidities and low supersaturations. The particle length (longest dimension) and their fractal dimension were determined before and after the humidification using scanning electron microscopy. Particles with an original mean length between 3 and 8 μm and a fractal dimension of $d_f \approx 1.78$ showed a shrinking by about 40% after an exposure to 97% RH, and their fractal dimension increased to 1.87. The restructuring was more pronounced at higher RH: Particles exposed to 2.9% supersaturation shrank by about 76% in length, and their fractal dimension increased to 2.5.

Figure 5 shows the growth factors obtained for combustion particles produced by a four-stroke spark ignition engine using leaded fuel. In these measurements, the particles were sampled using the cold dilution technique. Measurements with a hot dilution showed a similar behavior. It can be seen that combustion particles start to grow at about 95% RH. Even though the growth is much smaller than for the NaCl particles, it is significant. According to the Köhler model (which strictly applies only to spherical and completely soluble particles), the growth of combustion particles at subsaturation is caused by water-soluble material on the particle surface. Steiner et al. (23) showed that combustion particles from the same engine contain more than 90% volatile compounds. The growth behavior described above suggests that at least part of those compounds are water-soluble.

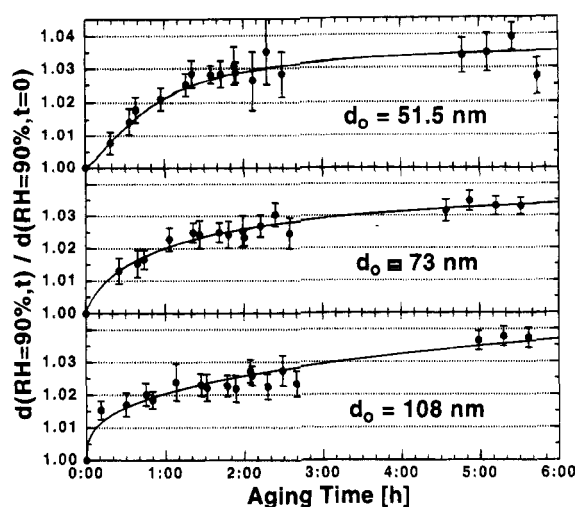


FIGURE 6. Growth factor $[d(\text{RH}=90\%, t) / d(\text{RH}=90\%, t=0)]$ of combustion particles after an aging time t . The solid lines are not theoretical curves; they are added to guide the eye.

In addition, Figure 5 shows that larger particles (with dry diameters $d_0 = 108$ nm) first shrink slightly and then start to grow at higher relative humidity. The fractal dimension of these particles before the humidification (again measured with a low pressure impactor) is very close to 3.0 (20). Thus, these particles exhibit a more compact structure than the spark discharge particles, which is also visible in transmission electron microscopy pictures (23). This explains why the combustion particles undergo less restructuring than the carbon particles produced by the spark discharge.

First investigations were also performed on aged combustion aerosols. A conductive bag (1.5 m^3) was filled with the exhaust gas of the engine by using the cold dilution technique. No additional gaseous compounds were added to the air in the bag, and there was no light inside the bag. Figure 6 shows the measured growth factors (at $\text{RH} = 90\%$) as a function of the aging time in the bag, normalized to the growth factor of the fresh particles at $\text{RH} = 90\%$. Obviously, the particles get more hygroscopic with increasing residence time in the bag and reach a growth factor of about 1.035 after 6 h. For larger particles, this occurs more rapidly than for smaller particles. Further experiments are planned in order to find out which chemical or physical processes are responsible for the observed changes in hygroscopicity, which finally lead to a growth factor of about 1.1 at $\text{RH} = 85\%$ as observed in ambient measurements (see ref 2).

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