Measurements of Hygroscopicity and Volatility of Atmospheric Ultrafine Particles during Ultrafine Particle Formation Events at Urban, Industrial, and Coastal Sites

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The tandem differential mobility analyzer (TDMA) technique was applied to determine the hygroscopicity and volatility of atmospheric ultrafine particles in three sites of urban Gwangju, industrial Yeosu, and coastal Taean in South Korea. A database for the hygroscopicity and volatility of the known compositions and sizes of the laboratory-generated particles was first constructed for comparison with the measured properties of atmospheric ultrafine particles. Distinct differences in hygroscopicity and volatility of atmospheric ultrafine particles were found between a “photochemical event” and a “combustion event,” as well as among different sites. At the Gwangju site, ultrafine particles in the “photochemical event” were determined to be more hygroscopic (growth factor (GF) = 1.05−1.33) than those in the “combustion event” (GF = 1.02−1.12), but their hygroscopicity was not as high as pure ammonium sulfate or sulfuric acid particles in the laboratory-generated database, suggesting they were internally mixed with less soluble species. Ultrafine particles in the “photochemical event” at the Yeosu site, having a variety of SO2, CO, and VOC emission sources, were more hygroscopic (GF = 1.34−1.60) and had a higher amount of volatile species (47−75%) than those observed at the Gwangju site. Ultrafine particle concentration at the Taean site increased during daylight hours with low tide, having a higher GF (1.34−1.80) than the Gwangju site and a lower amount of volatile species (17−34%) than the Yeosu site. Occasionally ultrafine particles were externally mixed according to their hygroscopicity and volatility, and TEM/EDS data showed that each type of particle had a distinct morphology and elemental composition.

Introduction

Ultrafine particles (<100 nm) in the ambient atmosphere are of current interest due to their effects on human health and atmospheric environments. Typically, these particles exist in large numbers and provide a high surface area-to-volume ratio, potentially leading to higher toxicity on human health (1−3). Ultrafine particles can also grow into cloud condensation nuclei (CCN), affecting cloud formation, and grow to sizes that are optically important, directly affecting the earth’s radiation balance (4). These particles are either directly emitted into the atmosphere from various sources, including fossil fuel and biofuel combustions, or are formed by gas-to-particle conversion processes such as nucleation and condensation. To better understand their formation pathways, sources, and effects on human health and climate forcing, it is essential to determine the physical and chemical properties of ultrafine particles in real time (5).

Determining the chemical composition of ultrafine particles in the ambient atmosphere, however, has been difficult due to their small size and mass and their rapid dynamic processes. The aerosol mass spectrometry techniques have allowed the chemical composition of particles to be measured in real time (6−9); however, depending on type of the aerosol mass spectrometry, the detectable size has been limited to only 50−200 nm. Using the tandem differential mobility analyzer (TDMA) technique to measure the hygroscopicity and/or volatility of ultrafine particles has made it possible to indirectly estimate the chemical composition of nanoparticles less than 50 nm (10−17). In addition, hygroscopicity plays an important role in the growth of cloud condensation nuclei, scattering efficiency (18), and particle transport behaviors. It also affects the deposition pattern of inhaled particles in the humid human respiratory system. Measurements of volatility will provide useful insights into volatile organic components in particles.

In this study, we apply the TDMA technique (10) to determine both the hygroscopicity and volatility of atmospheric ultrafine particles at three distinct sites in Korea: urban Gwangju, industrial Yeosu, and coastal Taean (Supporting Information (SI) Figure S1). When an elevated concentration of ultrafine particles was observed (i.e., ultrafine particle event), their hygroscopicity and volatility were measured to infer their possible formation mechanism or source. By comparing the hygroscopicity and volatility of ultrafine particles in similar ultrafine particle formation events (“photochemical event” and “combustion event”) (19) among different sites, the effects of local environments and sources on them were examined. Also, a database of hygroscopicity and volatility for ultrafine particles of known compositions and sizes was established. This is important for comparing the measured hygroscopicity and volatility of atmospheric ultrafine particles with those in the database to better infer the chemical composition of particles after accounting for their size. Elemental and morphological analyses of ultrafine particles were also carried out to better understand their composition and shape. Furthermore, PM10, NO2, CO, SO2, O3, and meteorological data were obtained at the sampling sites.

Materials and Methods

Measurements were conducted during the sampling periods of October 11−24, 2007 and May 5−18, 2008 at the Gwangju site, January 16−25, 2008 at the Yeosu site, and August 29 to September 5, 2008 at the Taean site. The urban Gwangju sampling site was located approximately 7.6 km north of the downtown Gwangju city hall and 4.2 km from the Hanam industrial complex. This area was influenced by a number of sources, including traffic from a nearby highway (1.5 km away from the site), heating systems from residential and commercial areas (0.6 km away from the site), and biomass burning from agricultural areas (0.8 km away from the site). The industrial Yeosu site was located 15 km away from the South Sea of Korea and 90 km southeast from the Gwangju
For atmospheric aerosol measurements, particles are passed through a PM2.5 inlet and are then dried by a Nafion drier (Nafion MD-110) before entering our instruments. Continuous measurements of particle size distributions from 20 to 600 nm were carried out by the regular SMPS (TSI 3081 DMA and TSI 3022A CPC). When an elevated ultrafine particle concentration was observed, the TDMA system was triggered to determine the hygroscopicity and volatility of the ultrafine particles, usually at peak mode diameter. The current TDMA system consists of two regular differential mobility analyzers (DMA, TSI 3081) (20), two nano differential mobility analyzers (nano DMA, TSI 3085) (21), an ultrafine condensation particles counter (UCPC, TSI 3776), a heated tube, and a humidification system, as shown in SI Figure S2. The combination of two nano DMAs and two regular DMAs enabled us to measure particle growth or shrinkage in a wide size range (5–680 nm).

The TDMA technique has been well illustrated in previous research (10, 13, 17, 22–24). In brief, particles are first dried to about 15% RH using a Nafion drier or a diffusion drier and passed through a 210Po “neutralizer”. Particles are then selected according to their mobility size by the first nano DMA or regular DMA. The selected particles of a certain size are sent into a humidifier or a heated tube and subsequently routed to the second nano or regular DMA and UCPC system to determine the amount of change in the particle size under the elevated relative humidity (85% RH) or increased temperature (100 °C) using an air conditioner. A fan was also operated and the material evaporated and subsequently cooled quickly upon exiting the furnace, causing homogeneous nucleation of the nanoparticles. TEM data showed that the particles produced from the furnace were not agglomerates. To look into the morphology and elemental composition of ultrafine particles, the size-selected particles were collected on a TEM grid using a nanometer aerosol sampler (TSI 3089). These samples were analyzed by transmission electron microscopy (TEM) (JEOL JEM-2100F) and energy dispersive spectroscopy (EDS) (OXFORD INCAx-sight).

**Results and Discussion**

The hygroscopicity and volatility of various laboratory-generated ultrafine particles of different sizes were tested using the TDMA technique. The hygroscopic GF at 85% RH and the volatile SF at the heater temperature of 100 °C for these particles are summarized in Figures 1 (a) and (b), respectively. As particle sizes decreased below 20–30 nm, the size-dependency of the GF became significantly more pronounced, particularly for sodium chloride, potassium chloride, and ammonium sulfate particles. A detailed explanation of the effects of particle size and structure on hygroscopic properties is available in our previous paper (31). The data shows that sodium chloride, ammonium sulfate, and sulfuric acid particles are “high-hygroscopic” (GF > 1.40), ammonium nitrate and malonic acid particles are “middle-hygroscopic” (1.20 < GF < 1.40), and C24, C32, glutaric acid, succinic acid, and soot particles are “low-hygroscopic” (GF < 1.20). Our measured growth factors of 50 nm ammonium sulfate (1.47 ± 0.05) and sodium chloride (2.00 ± 0.03) particles at 85% RH were consistent with previously reported values within 5% (27–30). They were also consistent with the theoretical values within 4%, after accounting for the Kelvin effect. In terms of volatility, as shown in Figure 1 (b), C24, dicarboxylic acids, and ammonium nitrate particles are completely volatile, whereas ammonium sulfate, sulfuric acid, sodium chloride, potassium chloride, magnesium chloride, calcium chloride, and soot particles are nonvolatile at the current heater temperature (100 °C). Figure 1 (b) also demonstrates that the C32 particles of 30 nm are completely volatile and the larger particles than 30 nm are semivolatile.

Continuous measurements of atmospheric particle size distributions, PM10, gas concentrations, T, and RH were
conducted at all three sampling sites. SI Table S1 summarizes this data including the GF, SF, and volume fraction of volatile species of the mode particles during ultrafine particle formation events. Typical examples of a diurnal variation of particle size distribution during (a) a photochemical event and (b) a combustion event are illustrated in SI Figure S3. When a strong solar radiation created a burst of ultrafine particles in the afternoon and increased O3 concentration, we classified this event as a photochemical event (SI Figure S3 (a)). On the other hand, when the increase of ultrafine particle concentration occurred in the morning and evening times and coincided with elevated NO2 and CO concentrations, this event was categorized as a combustion event (SI Figure S3 (b)).

Differences in the properties of ultrafine particles in a photochemical event versus a combustion event were examined by measuring their hygroscopicity and volatility. Figure 2 (a) shows the hourly variation of size distribution from 1 to 8 pm on October 16, 2007 at the urban Gwangju site when the photochemical event occurred. Nucleation mode particles started to form at around 1–2 pm with a mode diameter of 20 nm and gradually grew with a growth rate of 4.03 nm/hour until the nucleation mode particles disappeared at 5–6 pm. During this period of particle formation and growth, the ultrafine mode particles (i.e., 20, 25, and 30 nm) had a constant hygroscopic GF of 1.08 ± 0.04 and SF of 0.76 ± 0.02. The low GF suggests that the ultrafine particles contained a small amount of soluble species. Also, the constant GF and SF during that time period indicate that similar chemical species were continuously involved in the particle growth. In this case, the volume fraction of volatile species in the particle can be calculated from the SF assuming spherical particles, resulting in 56%. Note that for the candidate species tested, the sulfate particles were nonvolatile (i.e., the volume fraction of volatile species is 0%) whereas n-alkane and dicarboxylic acid particles were completely volatile at this temperature (100 °C), as shown in Figure 1.

Thus, such organic carbons would compose a significant portion of the volatile species. When the temperature of the heated tube increased to 200 °C, the atmospheric particles evaporated completely, suggesting that they contained no nonvolatile core like soot. Also, during this photochemical event, the O3 concentration significantly increased with low NO2, and CO concentrations compared to those in the combustion event, as included in SI Table S1.

FIGURE 1. (a) Hygroscopic growth factor at the RH of 85% and (b) shrinkage factor at the heater temperature of 100 °C for various laboratory-generated ultrafine particles.
Figure 2 (b) shows the hourly variation of particle size distribution in the combustion event occurring on May 8, 2008 at the Gwangju site. As shown in SI Table S1, NO2 and CO concentrations increased significantly during the combustion event, compared to the photochemical event or nonevent days. Ultrafine particles with a mode diameter of 80 nm appeared at 7 pm and the elevated concentration lasted until 11 pm. When the hygroscopicity and volatility of the mode particles were measured during this event, we observed two groups of particles with different GFs of 1.12 ± 0.06 and 1.47 ± 0.11, suggesting that the 80 nm particles were an external mixture of low-hygroscopic and high-hygroscopic species. The low-hygroscopic particles were more dominant with the relative number fraction of 71%. In terms of volatility, we observed only one group of particles having a SF of 0.95 ± 0.02, meaning that the low-hygroscopic and high-hygroscopic species had a similar volatility. TEM and EDS data for the mode particles collected during the same time period identified two major types of particles, as shown in SI Figures S4 (a) and (b). One group of particles was irregular or agglomerated and contained mostly C and O, as shown in SI Figure S4 (a). The other group of particles was spherical and contained C and S, as shown in SI Figure S4 (b). Thus, based on the TDMA and TEM/EDS data, we believe that an internal mixture of soot and organics could be a possible the group of particles having a GF of 1.12 ± 0.11 and a SF of 0.95 ± 0.02, whereas an internal mixture of organics and sulfates represents the group of particles having a GF of 1.47 ± 0.06 and a SF of 0.95 ± 0.02. Occasionally, particles were externally mixed according to their hygroscopicity and volatility. SI Table S2 summarizes the relative fractions of low-hygroscopic and high-hygroscopic, and “low-volatile” and “high-volatile” particles with their GFs and SFs when particles were externally mixed at the three sampling sites. Typically, in a photochemical event, the fraction of high-hygroscopic particles was greater than that of low-hygroscopic particles. In a combustion event, however, the fraction of low-hygroscopic particles was more abundant. The mixing of different air masses that contribute particles with different histories or multiple sources would cause the external mixing state of the particles (32).

The hygroscopicity and volatility of ultrafine particles for several photochemical events and combustion events observed at the Gwangju site are summarized in Figure 3. The
volatility is described by the volume fraction of the volatile species. The error bars represent the standard deviations of the GF and the fraction of volatile species during the event time period. In the case of an external mixture, the GF and the fraction of volatile species from the dominant group of particles were used. As shown in Figure 3, there is a distinct difference between the various photochemical events and combustion events for the ultrafine particles observed. The ultrafine particles in the photochemical events were more hygroscopic (GF = 1.05–1.33) compared to those in the “combustion events” (GF = 1.02–1.12), but their hygroscopicity was not as high as pure ammonium sulfate or sulfuric acid, as shown in Figure 1. This difference may be explained by the possible internal mixing of sulfates with nonhygroscopic or less hygroscopic species. The observed GF (1.05–1.33) in the photochemical event was less than the values (1.20–1.67) previously reported in urban areas (17), suggesting that the fraction of sulfate was smaller at the Gwangju site than other urban areas. We also found that the volume fraction of volatile species varied from day to day. Further, as the fraction of volatile species in the particles increased, the hygroscopic growth factor decreased, suggesting that the volatile species were nonhygroscopic. Our hygroscopicity and volatility data suggest that the ultrafine particles in the photochemical events at the Gwangju site are an internal mixture of sulfates and organics with a varying fraction of volatile organic species. We believe that secondary aerosol production under strong photochemical activity contributed to the formation of these ultrafine particles in the photochemical events.

A similar analysis was carried out for the ultrafine particles observed at the Yeosu site and the Taean site. Figure 4 compares the GF and the volume fraction of the volatile species in photochemical events among the three different sites and identifies a clear difference among them in terms of the hygroscopicity and volatility of ultrafine particles. The ultrafine particles at the Yeosu site were more hygroscopic than those observed at the Gwangju site and had a higher amount of volatile species than those of the Taean site. The measured GF and the volume fraction of volatile species varied from 1.34 to 1.60 and from 47 to 75%, respectively at the Yeosu site. The observed GF (1.34–1.60) was similar to values (1.20–1.67) previously reported in other urban areas (17). The Yeosu site is located in a highly polluted area affected by several industrial sources producing a variety of SO$_2$, CO, and VOC emissions. As shown in SI Table S1, the enhanced ultrafine particle concentration was observed when the air mass came from the northern areas where these industrial sources were located. Additionally, SO$_2$ and CO concentrations were higher at the Yeosu site than other sites and these increased levels of emissions tended to form condensing sulfuric acid and organic vapors. One example for diurnal variation in the number of ultrafine particles, SO$_2$, and CO concentrations at the Yeosu site is shown in Figure 5. The peak time of ultrafine particle concentration coincided with the peak concentrations of SO$_2$ and CO. Contrary to the similar events at the Gwangju site, the increasing fraction of volatile species with decreasing GF was not observed at the Yeosu site, suggesting that the volatile fraction at Yeosu contained some hygroscopic soluble species. By comparing the hygroscopicity and volatility of the ultrafine particles in similar ultrafine particle formation events (photochemical event) among the different sites, we investigated the effects of local environments and sources on the hygroscopicity and volatility of ultrafine particles. However, seasonal variation of hygroscopicity and volatility of ultrafine particles was not examined here and remains for future works.

Ultrafine particle events at the Taean site occurred during daylight hours with a low tide and exposed shorelines, similar to the nucleation event observed at a coastal marine site (33). As shown in Figure 4, the ultrafine particles observed at the Taean site during photochemical events are more hygroscopic (GF = 1.34–1.80) than those at the Gwangju site and have a smaller amount of volatile species (17–34%) than those at the Yeosu site. The measured GF was within the values (1.24–2.14) previously reported in marine environments (17). The absence of anthropogenic local sources is the primary cause of the low amount of anthropogenic volatile species and the higher growth factor is due to the abundance of salt particles in the clean marine environment. The GF, however, was still lower than that of pure sea salt, suggesting that condensation of semivolatile compounds onto the sea salt or inhomogeneous composition of ultrafine particles was responsible for the hygroscopicity being lower than pure sea salt particles (34). Previous findings showed that ultrafine particles in a marine environment can contain substantial organic fractions that were produced from the blooming of phytoplankton (34, 35). The Taean site is located in a coastal area, just 0.2 km away from the Yellow Sea of Korea, and the ultrafine particle events were observed during the day, coinciding with the low tide in late summer and early fall.

In the current study, the heater temperature was fixed at 100 °C to clearly discriminate sulfates (nonvolatile) and organic carbons (volatile) at this temperature. To provide better insight into the composition of volatile organic species, the heater temperature was occasionally varied. Figure 6 shows the size-change ($\Delta D_p = \Delta D_{p0}$) of the mode particles (30 nm on September 2, 2008, and 80 nm on September 3, 2008 at the Taean site, 20 nm on October 16, 2008 at the Gwangju site, and 30 nm on January 18, 2008 at the Yeosu site) as they
correspond with increases in the heater temperature. Based on the particle shrinkage of 30 nm particles and 80 nm particles at 100 °C at the Taean site, the calculated fraction of volatile species was similar for both aerosols. The composition of volatile species, however, should differ significantly due to the different slopes of decreasing size with increasing temperature. For 30 nm particles, the slope was not as steep as the 80 nm particles, suggesting that they have relatively less volatile species. Condensation of low volatility organic species produced by oxidation of volatile biogenic organic species can contribute to the volatile fraction of the 30 nm particles (34). For 80 nm particles, their volatile species evaporated at temperatures below 50 °C. At temperatures above 50 °C no more size change was observed from temperature increases. The GF of the 80 nm particles was 2.14 at this time, suggesting that the 80 nm particles have a core consisting of hygroscopic salt particles coated with a highly volatile species, which can be evaporated below 50 °C. For the case of 20 nm (Gwangju) and 30 nm particles (Yeosu), the similarities in slope suggest that the composition of volatile species is similar, even though the volatile fraction differs.

In conclusion, the TDMA technique was applied to determine the hygroscopicity and volatility of laboratory-generated particles of known sizes and compositions, along with atmospheric ultrafine particles at urban Gwangju, industrial Yeosu, and coastal Taean sites in Korea. The database for the hygroscopicity and volatility of laboratory-generated particles has enabled us to compare them with the measured properties of atmospheric ultrafine particles. A comparison of the hygroscopicity and volatility of ultrafine particles in similar ultrafine particle formation events (photochemical event) among the different sites has shown a clear difference in the hygroscopicity and volatility of the ultrafine particles, suggesting that their source and formation pathway varied among the sites. The TEM/EDS analysis also showed different morphology:

![Figure 5](image1.png)

**FIGURE 5.** Diurnal variation of ultrafine particle number concentration (N(13-100 nm)), CO, and SO2 in a photochemical event at the Yeosu site (1/17/2008).

![Figure 6](image2.png)

**FIGURE 6.** Size-change (\(D_{p2} - D_{p1}\)) of ultrafine particles as a function of heater temperature (30 nm on September 2, 2008, and 80 nm on September 3, 2008 at the Taean site, 20 nm on October 16, 2008 at the Gwangju site, and 30 nm on January 18, 2008 at the Yeosu site).
and elemental composition of ultrafine particles that are externally mixed according to their hygroscopicity and volatility.

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Supporting Information Available

Map of sampling sites, a schematic of the TDMA system, diurnal variation of particle size distribution, TEM/EDS data, and summary tables for hygroscopicity and volatility. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


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