This article was downloaded by: [Korea Polar Research Institute], [Young Jun YOON]
On: 23 October 2013, At: 18:23
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Aerosol Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uast20

# Mixing State of Size-Selected Submicrometer Particles During Photochemical and Combustion Events Measured with the Tandem System

Jaeseok Kim [a c] , Shila Maskey [a] , Young Jun Yoon [b] & Kihong Park [a]

[a] School of Environmental Science and Engineering, Gwangju Institute of Science and Technology , Buk-gu , Gwangju , Republic of Korea

[b] Korea Polar Research Institute, Get-Pearl Tower , Yeonsu-Gu , Incheon , Republic of Korea

[c] Department of Applied Physics , University of Eastern Finland , Kuopio , Finland

Accepted author version posted online: 29 Mar 2013.Published online: 14 Apr 2013.

To cite this article: Jaeseok Kim , Shila Maskey , Young Jun Yoon & Kihong Park (2013) Mixing State of Size-Selected Submicrometer Particles During Photochemical and Combustion Events Measured with the Tandem System, Aerosol Science and Technology, 47:7, 746-754, DOI: 10.1080/02786826.2013.789822

To link to this article: http://dx.doi.org/10.1080/02786826.2013.789822

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

*Aerosol Science and Technology*, 47:746–754, 2013
Copyright © American Association for Aerosol Research
ISSN: 0278-6826 print / 1521-7388 online
DOI: 10.1080/02786826.2013.789822

# Mixing State of Size-Selected Submicrometer Particles During Photochemical and Combustion Events Measured with the Tandem System

**Jaeseok Kim,[1,3] Shila Maskey,[1] Young Jun Yoon,[2] and Kihong Park[1]**
[1]*School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Buk-gu, Gwangju, Republic of Korea*
[2]*Korea Polar Research Institute, Get-Pearl Tower, Yeonsu-Gu, Incheon, Republic of Korea*
[3]*Department of Applied Physics, University of Eastern Finland, Kuopio, Finland*

**A tandem differential mobility analyzer (TDMA) was applied to determine the mixing state of size-resolved submicrometer particles, in an urban area of Gwangju in Korea, when enhanced concentrations of particles were observed (e.g., photochemical and combustion events). The existence of a nonvolatile core was identified after removing volatile species with increasing temperature up to ∼250°C. Data showed that in the combustion event, the accumulation mode particles (137–139 nm) increased significantly and they had a nonvolatile core coated with volatile species, while in the photochemical event, the nucleation mode (15–30 nm) particles enhanced and there was no such nonvolatile core (i.e., they were completely evaporated below 250°C). When hygroscopic growth factor (HGF) of the core particles was measured in the combustion event, their values were close to one, suggesting that they consist of nonvolatile and nonhygroscopic species like black carbon. In the photochemical event, the nucleation mode particles were completely evaporated at 250°C and had some volatile fractions at 100°C, unlike pure ammonium sulfate, and had C and S elements in their TEM/EDS data, suggesting that they have an internal mixture of sulfate and organics. Also, the HGF of the remaining particles after removing volatile species at 150°C increased, but not as much as expected for the case of complete evaporation of volatile species at this temperature. Data for evaporative behaviors of laboratory-generated aerosols (i.e., ammonium sulfate and succinic acid) suggest that evaporation of volatile species in a well-mixed mixture was delayed compared to those existing as single species.**

## 1. INTRODUCTION

Atmospheric aerosols affect earth's radiation budget directly by absorbing and scattering incoming sunlight and indirectly by acting as cloud condensation nuclei (CCN) to form clouds (Charlson et al. 1992; Lightstone et al. 2000; Kanakidou et al. 2005; IPCC 2007). Aerosols also influence visibility degradation (Seinfeld and Pandis 1998) and human health (Zimmermann 2011; Bakand et al. 2012) and are involved in various heterogeneous chemical reactions in the ambient atmosphere (Seinfeld and Pandis 1998). Typically, atmospheric particles are directly emitted from anthropogenic and natural sources such as vehicles, industrial factories, biomass burning, oceans, and deserts. Also, atmospheric particles are produced indirectly by gas-to-particle conversion processes (Andreae 2007, 2009). Due to multiple sources and various aging processes (e.g., condensation, coagulation, oxidation, and cloud processing) for atmospheric particles, they exist in various mixing states having multiple chemical constituents. For instance, particles can be externally mixed (each particle consists of a single chemical species) or internally mixed (particles consist of a mixture of various chemical species) (Zhang et al. 1993; Bond and Bergstrom 2006; Péré et al. 2009). The internal mixture can further be classified into "well-mixed" and "core-shell" mixtures (Jacobson 2001; Bond and Bergstrom 2006). "Well-mixed" is a mixture where multiple components exist in a well-mixed state, while "core-shell" is a mixture where a solid core is coated by different chemical species.

Recently, the mixing state of atmospheric aerosols has been considered an important input parameter into climate models to better predict the impact of aerosols on climate change (Koloutsou-Vakakis et al. 1998; Satheesh et al. 2006; Satheesh et al. 2008; Riemer et al. 2009; Park et al. 2011). It was reported that black carbon (BC) particles coated by liquid species (i.e., core-shell mixture) led to enhanced absorption of incoming solar light compared to pure BC particles (Jacobson 2000, 2001; Chandra et al. 2004; Mikhailov et al. 2006; Moffet and Prather

---

Received 3 December 2012; accepted 10 March 2013.

The research described in this article was supported by the National Leading Research Laboratory program funded by Korean Government (NRF-2011-0015548) and the National Research Foundation of Korea Grant funded by the Korean Government (NRF-2011-0021066).

Address correspondence to Kihong Park, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, 1 Oryong-dong, Buk-gu, Gwangju 500712, Republic of Korea. E-mail: kpark@gist.ac.kr

2009). Xue et al. (2009) showed that coating soot particles with dicarboxylic acids (i.e., core-shell mixture) led to enhanced light scattering efficiency. Freney et al. (2010) reported that light scattering efficiency of internal mixtures having nonspherical particles in aqueous droplets was higher than that of core-shell particles. In addition to the optical property changes of particles depending on the mixing state, the hygroscopic property of particles, which is an effective indicator for CCN, was also affected by their mixing state. The hygroscopicity of a well-mixed mixture of dicarboxylic acids and ammonium sulfate was reported to be lower than pure ammonium sulfate particles and higher than pure dicarboxylic acid particles having the same volume (Hämeri et al. 2002; Prenni et al. 2003; Wise et al. 2003). When the nonhygroscopic BC particles were coated by hygroscopic species, the BC particles became hygroscopic, leading to a lifetime reduction of the BC particles due to wet scavenging in the ambient atmosphere (Xue et al. 2009). The change in hygroscopicity of the coated BC particles can also affect cloud formation and the deposition pattern in the human respiratory system.

Several previous studies have reported on the mixing state of atmospheric particles (Adachi and Buseck 2008; Péré et al. 2009; Adachi et al. 2011). It was reported that sulfate and organic particles in Los Angeles were externally mixed for the given size of 50–300 nm, whereas particles sampled in Mexico City were reported to be internal mixtures of sulfate and weakly hygroscopic organic species (Adachi et al. 2011). Based on microscopic analysis of particles sampled in the plume in Mexico City, Adachi and Buseck (2008) found that more than 50% of the collected particles had a core-shell mixture (i.e., soot particles were coated with organic matter and sulfate). Péré et al. (2009) reported that the core-shell mixture (e.g., soot or dust particles were coated by secondary organic species) was the most probable mixing state of atmospheric aerosols emitted from biomass burning and anthropogenic sources over Europe during summer of 2003. In the Indo-Gangetic Plain of India, it was observed that the mixing state of atmospheric aerosols varied with the season (Dey et al. 2008; Srivastava and Ramachandran 2013). However, few studies have reported on the mixing state of size-resolved particles during specific ultrafine particle formation events.

In this study, the mixing state of size-selected submicrometer particles was determined by using a hygroscopicity tandem differential mobility analyzer (HTDMA) system with a thermodenuder or volatility hygroscopicity TDMA (VH-TDMA) (Rader and McMurry 1986; Johnson et al. 2004; Park et al. 2008; Villani et al. 2008; Park et al. 2009b) during particle formation events (photochemical event or combustion event) in an urban area of Gwangju in Korea. This online measurement technique will overcome the limitation of microscopic techniques such as low particle counting statistics and evaporative artifacts (e.g., evaporation of volatile species during microscopic analysis). In this technique, the existence of nonvolatile cores was identified after removing volatile species using the thermodenuder by increasing the temperature to ∼250°C. Also, hygroscopicity of the core particles (i.e., the remaining particles after evaporation of any volatile species at ∼250°C) was measured to estimate the chemical constituents of the core particles. In the absence of a nonvolatile core, the change of hygroscopicity of particles at varying temperatures (25–250°C) was determined. The HTDMA system without the thermodenuder was used for determination of the external mixing state of size-selected particles with different hygroscopic species.

## 2. EXPERIMENTAL METHODS

Measurements were conducted in an urban area of Gwangju (35° 13’N 126° 50’E) in Korea from 18 July to 14 September 2011. The sampling site was located around a residential area (∼0.6 km away), an agricultural area (∼0.8 km away), a highway (∼1.5 km away), and a small industrial complex (∼4 km away) (Park et al. 2008). The atmospheric particles first passed through a $PM_{10}$ inlet, which was placed on the rooftop of a four-story building (approximately 15 m above ground level). The particles were dried out using a series of diffusion dryers (TSI 3062; TSI Inc., Shoreview, MN, USA) before entering an aerosol measurement system. A scanning mobility particle sizer (SMPS; TSI 3081 DMA and TSI 3022A CPC) was used to continuously measure the size distribution of particles from 15 nm to 600 nm. Hourly $O_3$, $NO_2$, CO, and $SO_2$ concentration data were obtained at a nearby sampling site.

Particle formation events when a significant increase in number concentration of submicrometer particles (10–100 nm or 10–200 nm) occurred were classified into “photochemical” and “combustion” events. When the increase of concentration of submicrometer particles was consistent with $O_3$ and solar radiation, this event was classified as a photochemical event. When the increase of particle concentration coincided with elevated $NO_2$ and CO concentrations, this event was classified as a combustion event. When these particle formation events occurred (i.e., photochemical and combustion events), the thermodenuder-HTDMA system was triggered to determine the mixing state of size-selected particles (i.e., the nucleation or accumulation mode particles). The thermodenuder-HTDMA system mainly consists of three differential mobility analyzers (DMAs) (Knutson and Whitby 1975; Chen et al. 1998), a condensation particle counter (CPC, TSI 3010), a humidification system, and a thermodenuder (heated tube and charcoal absorber), as shown in Figure 1. Three DMAs were used to cover a wide dynamic size change under an elevated temperature. The temperature varied from 25–250°C. For hygroscopic growth measurement, the RH was fixed at 85%. The tandem measurement technique is described well in previous studies (Rader and McMurry 1986; McMurry and Stolzenburg 1989;

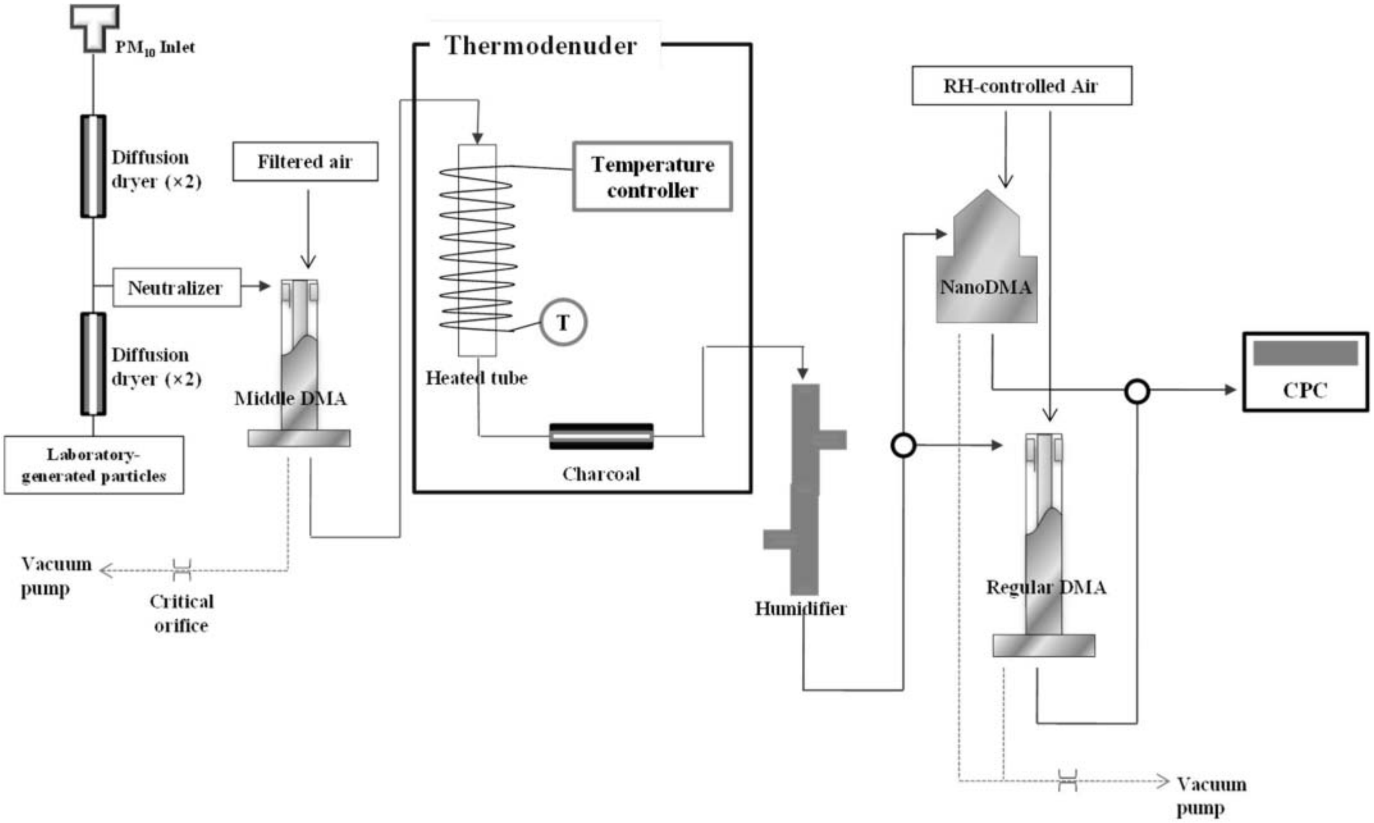

FIG. 1. A schematic of the experimental setup.

Sakurai et al. 2003; Rose et al. 2006; Park et al. 2009a). The experimental procedure is given ahead.

To measure shrinkage factor (SF; the ratio of particle mode diameter at increased temperature to that at room temperature) of particles and to identify the existence of nonvolatile core in them, ambient particles were first dried using a series of diffusion driers and passed through a $^{241}$Am "neutralizer" before being selected by the first DMA (the mode particles identified by the SMPS was selected). The selected particles were directly introduced to the humidifier at room temperature (25°C) and dry condition ($<$10% RH) without passing through the thermodenuder. The resulting size distribution was measured with the second DMA and CPC, which provides particle mode diameter at room temperature and dry condition. While the particle size distribution was being measured at the dry condition, the heater temperature in the thermodenuder system increased to 100°C to minimize a waiting time to increase the temperature. Then, the selected particles by the first DMA were introduced to the thermodenuder. The residence time for particles through the heated tube is 270 ms. The size distribution of the remaining particles after removing volatile species at 100°C was measured with the second DMA and CPC. The heat temperature further increased to 150°C, 200°C, and 250°C, and at each temperature, the resulting size distribution was measured in a similar manner to above, providing the SF as a function of the heater temperature. If the particles are completely evaporated at 200–250°C, no particles will be detected, which is the case for ammonium sulfate, ammonium bisulfate, ammonium nitrate, sulfuric acid, C24-C32, and dicarboxylic acids based on our laboratory measurements. If particles exist after removing volatile species at 250°C, they should have a nonvolatile core. In this way, the existence of nonvolatile core in the size-selected particles can be verified. The volume fraction of core particles is calculated from the SF assuming spherical particles. Laboratory tests excluded the possibility of recondensation of evaporated species in the thermodenuder-HTDMA system.

To measure hygroscopic growth factor (HGF) of the particles after being heated up to 150–250°C, particles after shrinkage were exposed to the elevated RH (85%). In the SF measurements in the previous section, the RH was kept at low humidity ($<$10%) by supplying dry sheath air passing through diffusion dryers and a filter to the humidifier and the sheath air of second DMA. A mixture of wet and dry air was supplied by mass flow controllers to the humidifier and the sheath air of the second DMA to obtain 85% RH. The RH and temperature were measured at downstream of the humidifier and the excess air of the second DMA. The room temperature was controlled to maintain 25°C; a small fan was used to remove any hot spot of the tube after the humidifier. The time for obtaining stable RH (i.e., 85%) with this method was less than 5 min (only one RH condition was used in this study). The HGF of 20 nm ammonium sulfate at 85% RH was ~1.40, which is close to reported (1.44) value with the Kelvin correction (Biskos et al. 2006). In the combustion event, the HGF of the particles after being heated to 250°C (i.e., nonvolatile core) was measured, while in the photochemical event, the HGF of the particles after being heated to 150°C was measured. The HGF of the particles was derived as the ratio of particle mode diameter at the given temperature of the thermodenuder and RH (85%) to particle mode diameter at the same thermodenuder temperature as above and RH (<10%). At each condition, 4–5 data points were obtained and the whole measurements were completed within 1–2 h after particle formation events appeared. If the size-selected particles exist in an external mixing state, two or more groups of particles having different HGFs after humidification or SFs after heating will appear.

Various laboratory-generated aerosols are produced using an atomizer and furnace reactor system; their HGF and SF were determined by the thermodenuder-HTDMA system. For production of an internal mixture of particles in well-mixed state, an aqueous solution was prepared by homogeneously mixing known amounts of target species in deionized water and then aerosolized via an atomizer (TSI 3076, USA). To examine the morphology of atmospheric particles, they were collected on a transmission electron microscopy (TEM) grid using a nanometer aerosol sampler (TSI 3089; Dixkens and Fissan 1999). These samples were analyzed using TEM (JEOL JEM-2100F; JEOL Ltd., Akishima, Tokyo, Japan) and EDS (OXFORD INCA x-sight; Oxford Instruments plc; Abingdon, Oxfordshire, UK).

## 3. RESULTS AND DISCUSSION

Hourly variation of particle size distribution in the combustion event occurring on 31 August 2011 is shown in Figure 2a. The number of particles increased at 8:00 PM with a mode diameter of ~137 nm; the elevated concentration lasted until 11:00 PM. As shown in Figure 2b, the increase of N (10–200 nm) coincided with $NO_2$, suggesting that those particles were produced from combustion sources. When the hygroscopicity and volatility of the mode particles were measured during this event, the particles had an average HGF of 1.16 ± 0.03 at 85% RH and an SF of 0.92 ± 0.01 at 100°C, suggesting that they had both hygroscopic species (but not highly hygroscopic) and volatile species (~22% volume fraction). TDMA data for the mode particles suggested that they were not significantly externally mixed with different hygroscopic or volatile species (i.e., only one peak in the size distribution at 85% RH or 100°C). In order to examine the mixing state of the mode particles (130–140 nm) in the combustion events, they were introduced to the thermodenuder and exposed to varying temperatures; the SF of the mode particles as a function of temperature is shown in Figure 3. As shown, volatile species evaporated from 50°C up to 200°C, and after that, no significant size change was observed by further increasing the temperature. This suggests that those particles contain a nonvolatile core and exist in a core-shell mixing state. The volume fraction of the core was calculated as 36–41%,

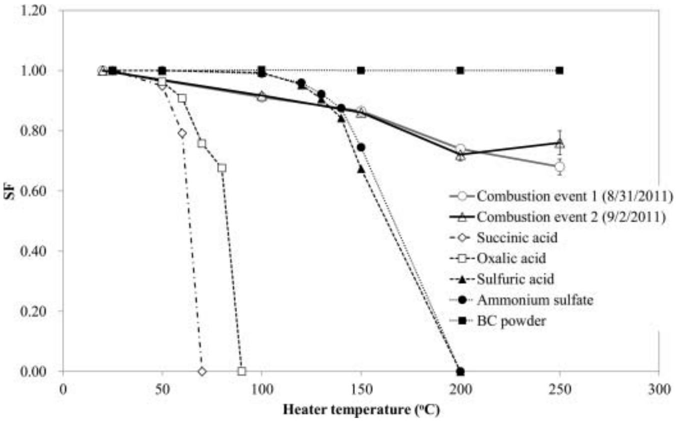

FIG. 3. SFs of the accumulation mode particles (137 nm on 31 August 2011 and 139 nm on 2 September 2011) in combustion events and laboratory-generated particles (succinic acid, oxalic acid, sulfuric acid, ammonium sulfate, and BC) as a function of temperature.

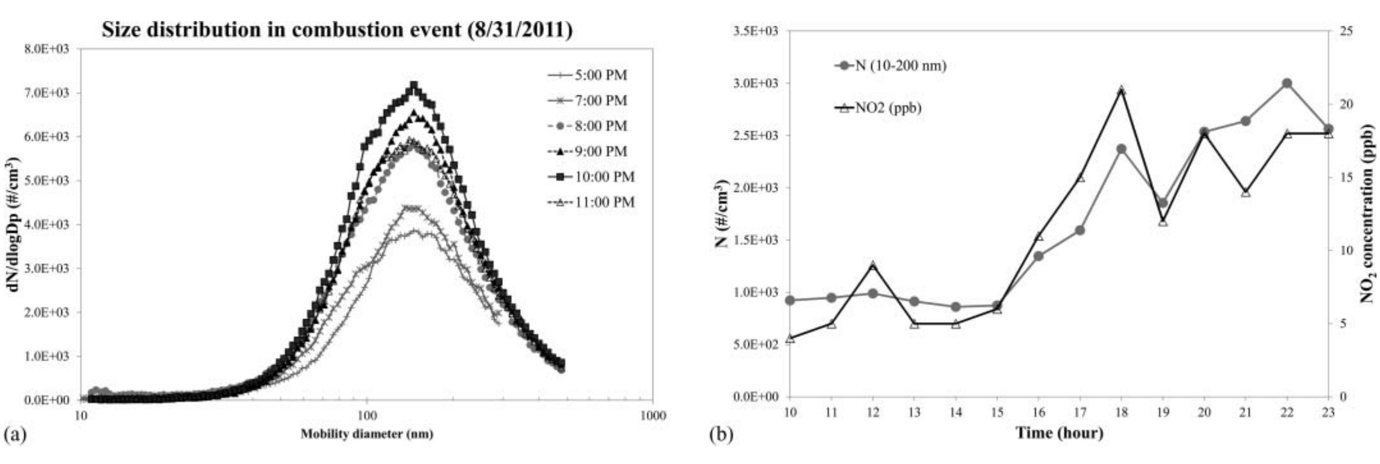

FIG. 2. (a) Variation of hourly average particle size distribution and (b) diurnal variations of N (10–200 nm) and $NO_2$ (ppb) in the combustion event on 8/31/2011.

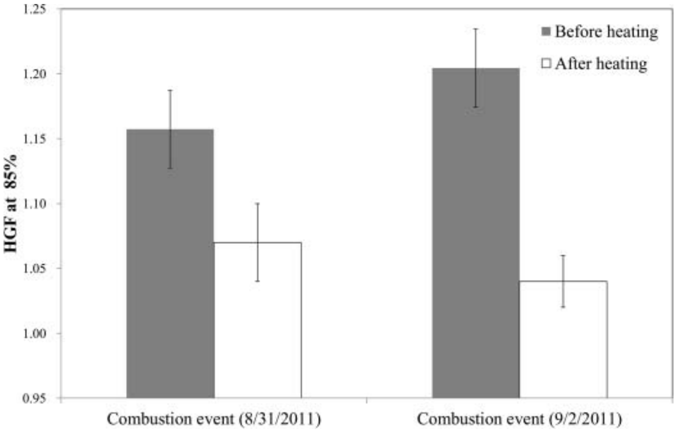

FIG. 4. HGFs of particles before and after heating of the accumulation mode particles (137 nm on 31 August 2011 and 139 nm on 2 September 2011) at 250°C in combustion events.

assuming they are spherical particles. For comparison, data for BC, succinic acid, oxalic acid, sulfuric acid, and ammonium sulfate particles were included. The sulfuric acid may be neutralized to ammonium sulfate or ammonium bisulfate (Johnson et al. 2005; Grose et al. 2006; Biskos et al. 2009). No size change was observed for pure BC particles up to 250°C, while oxalic acid, succinic acid, sulfuric acid, and ammonium sulfate particles were completely evaporated by increasing the temperature to 200°C.

When the hygroscopic property of the core particles after removing volatile species at 250°C was measured, the HGF decreased compared to the mode particles before removing volatile species as shown in Figure 4. For particles observed in the combustion event, the Kelvin effect (the HGF decreased with decreasing size) was not significant due to their large size (>90 nm) (Park et al. 2009a). The HGFs of the core particles were close to 1.0, suggesting that the core mostly consists of nonhygroscopic species like BC or soot particles. TEM images of particles observed in the combustion event are shown in Figure 5. Submicrometer particles having a core-shell mixing state were also identified in the TEM images. When a single particle was magnified via an intensified electron beam, it was observed that the coated species were evaporated (Tumolva et al. 2010). As can be seen, the core particles are not spherical and sometimes they are agglomerated. It is possible that a morphological change of the particles (i.e., from spherical to nonspherical) during heating can lead to different values of the core volume fraction from those calculated by mobility size change, assuming that particles are spherical before and after heating (Zhang et al. 2008). By assuming that particles became a compact cluster (dynamic shape factor = 1.17) from a spherical shape after evaporation of volatile species, the core volume fraction decreased by 23% compared to value calculated by assuming that particles were sphere.

Hourly size distribution of particles in the photochemical event (14 September 2012) as a function of time is shown in Figure 6a. Nucleation mode particles started to form at around 12:00–1:00 PM with a mode diameter of ∼15 nm and gradually grew with a growth rate of 4.8 nm $h^{-1}$ until the nucleation mode particles disappeared. As shown in Figure 6b, the time for increased concentration of N (10–100 nm) coincided well with $O_3$ and solar radiation, suggesting that these ultrafine

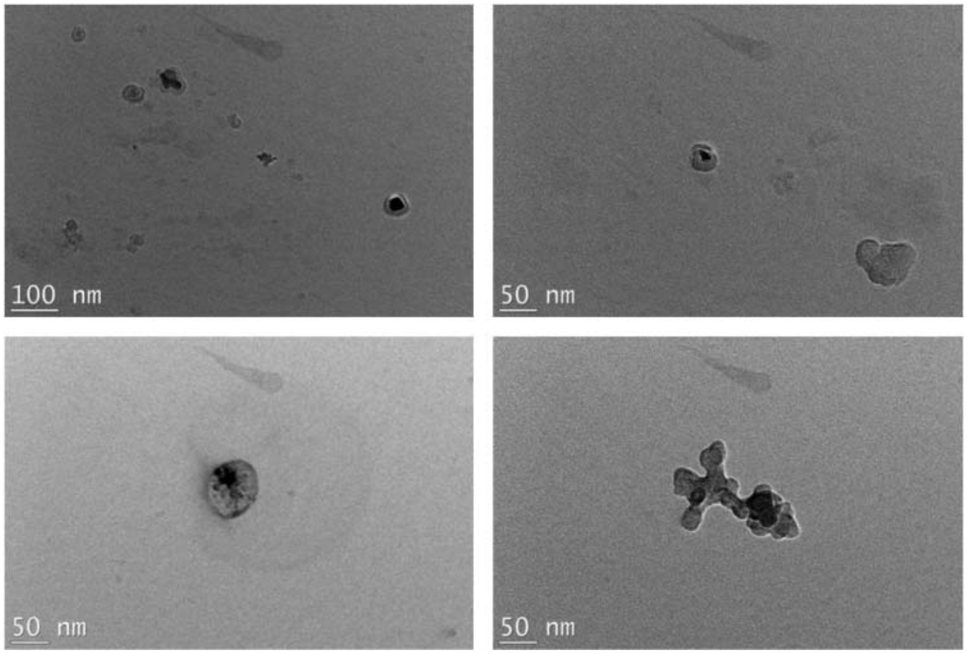

FIG. 5. TEM images of submicrometer particles observed in the combustion event.

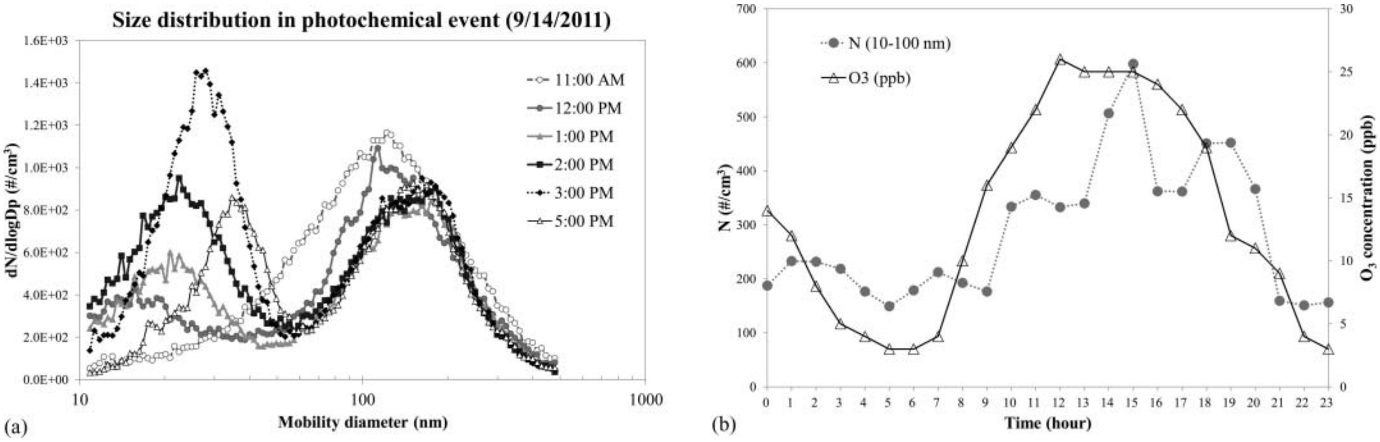

FIG. 6. (a) Variation of hourly average particle size distribution and (b) diurnal variations of N (10–100 nm) and $O_3$ (ppb) in the photochemical event on 14 September 2011.

particles were produced by photochemical activity. During the period of particle formation and growth from 15 nm to 30 nm, the 20 nm particles were selected to measure the HGF (85% RH) and SF (100°C). They had a constant HGF of 1.24 ± 0.02 and SF of 0.95 ± 0.002 without significant external mixing of different hygroscopic or volatile species. The volume fraction of volatile species in the particle was ~14% at a heater temperature of 100°C. The constant HGF and SF during that time period indicate that similar chemical species (possibly sulfate and organics) were continuously involved in the particle growth.

The SF of the mode particles (20 nm on 13 September 2012 and 30 nm on 14 September 2011) as a function of temperature in photochemical events is shown in Figure 7. When the temperature increased to 200°C, the particles were completely evaporated, suggesting that they contained no nonvolatile core such as those found in the combustion event as discussed previously. Their evaporative behavior is similar to that of ammonium sulfate. However, the ambient particles had some volatile fraction (13~24% volume fraction) at 100°C contrary to those of pure ammonium sulfate or sulfuric acid, suggesting that they are internal mixtures of sulfate and organics. TEM images of submicrometer particles observed in the photochemical event are shown in Figure 8. They had C and S elements, also suggesting that they are internal mixtures of sulfate and organics. When a single particle was magnified using an intensified electron beam, it was observed that most species were evaporated (i.e., no nonvolatile core).

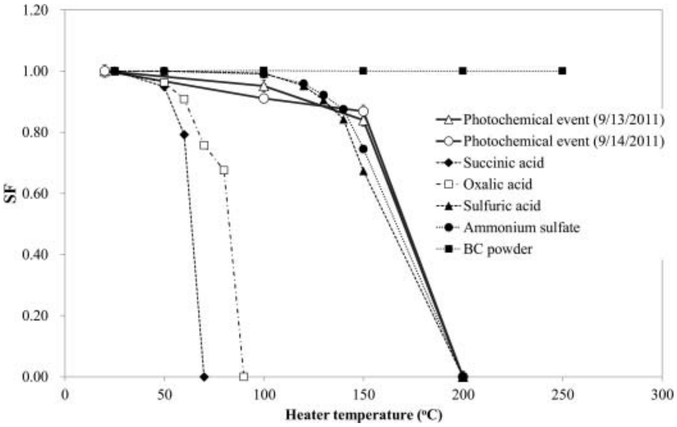

FIG. 7. SFs of the nucleation mode particles (20 nm on 13 September 2011 and 30 nm 14 September 2011) in photochemical events and laboratory-generated particles (succinic acid, oxalic acid, sulfuric acid, ammonium sulfate, and BC) as a function of temperature.

Before and after heating (150°C) of the mode particles (20 nm on 13 September 2012 and 30 nm on 14 September 2011) in photochemical events, the HGFs were compared as shown in Figure 9. The HGFs of particles after removing some volatile species increased compared to those before removing volatile species, which is contrary to those in combustion events. It is possible that the size difference before and after heating for particles observed in the photochemical event can cause the difference in the HGF due to their small size (<30 nm; i.e., Kelvin effect). However, the HGF increased after heating, and thus this cannot be due to the change of size (Michaud et al. 2009). Data suggest that volatile species that were less hygroscopic were evaporated at 150°C, leading to the higher HGF. Note that our laboratory measurements showed that pure organic species (e.g., *n*-alkanes [C24–C32] and dicarboxylic acids) were completely evaporated at 100°C. Thus, the HGF of particles at a heater temperature of 150°C should be much higher than the current value, if such less hygroscopic organic species were completely evaporated from the internal mixture of sulfate and organics. Volatile species existing in an internal mixing state in the photochemical event were not evaporated like they exist as pure species possibly due to their lowering vapor pressure (i.e., solute effect on vapor pressure). A similar result was observed for a mixture of ammonium sulfate and MSA (Johnson et al. 2004). To test the above hypothesis, pure ammonium

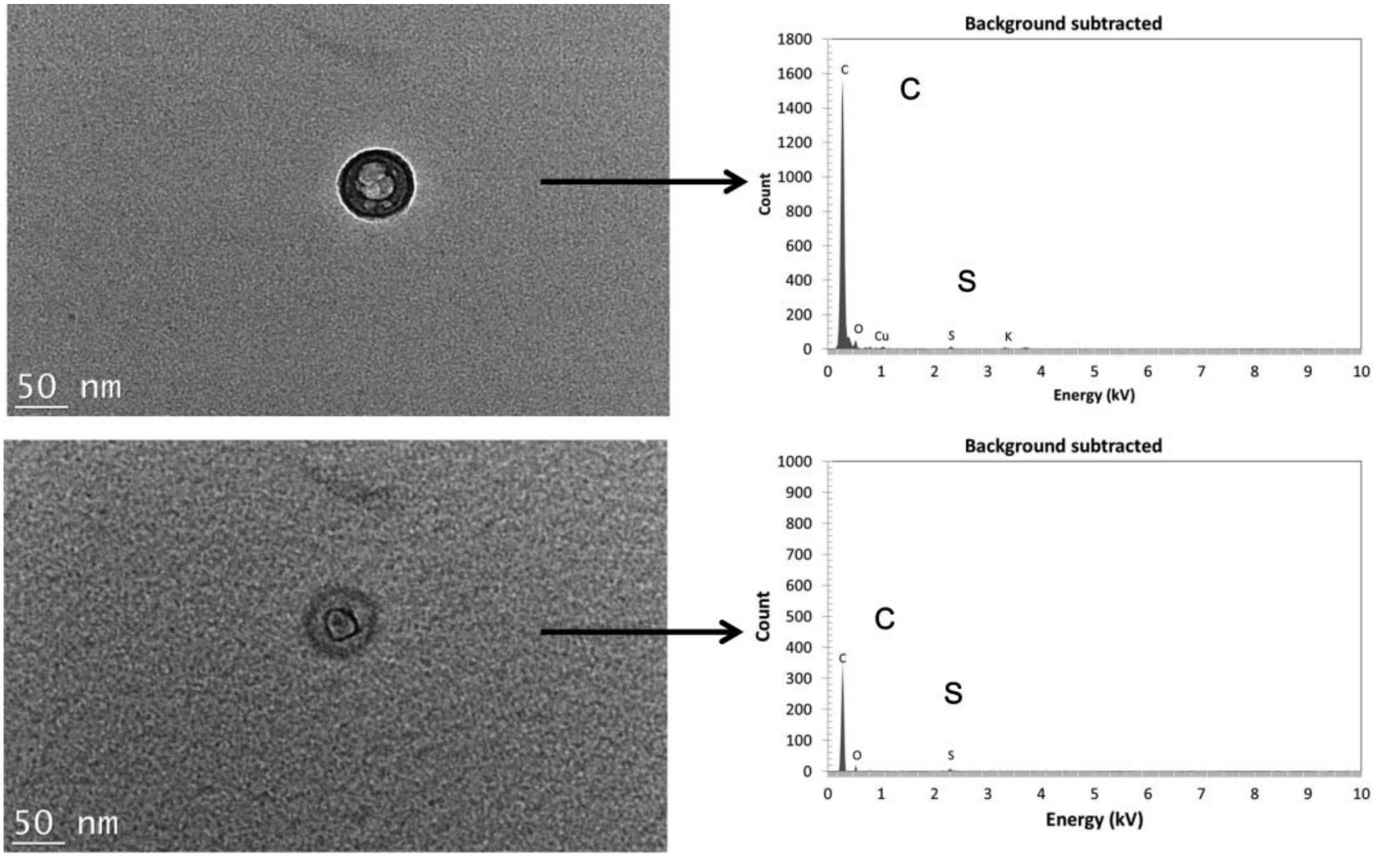

FIG. 8. TEM and EDS data for submicrometer particles observed in the photochemical event.

sulfate, pure succinic acid, and an internal mixture of ammonium sulfate and succinic acid (50%/50%) (in a "well-mixed" state) were produced and evaporative behaviors of the size-selected particles (∼30 nm) were examined as shown in Figure 10. As shown, the succinic acid as an internal mixture was not completely evaporated before 100°C unlike pure succinic acid, suggesting that the evaporation of the succinic acid as an internal mixture was delayed due to the mixing effect (e.g., lowering vapor pressure), which is a similar behavior to atmospheric ultrafine particles that have an internally mixed sulfate and organics in the photochemical event or nucleation event (Ristovski et al. 2010). When the volume fraction of volatile

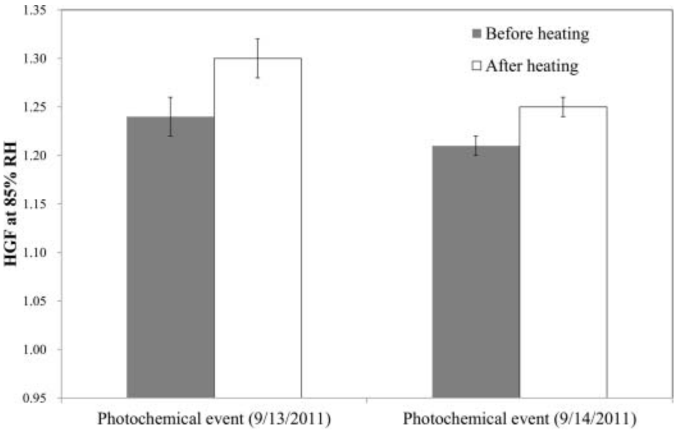

FIG. 9. HGFs of the nucleation mode particles (20 nm on 13 September 2011 and 30 nm 14 September 2011) before and after heating at 150°C in photochemical events.

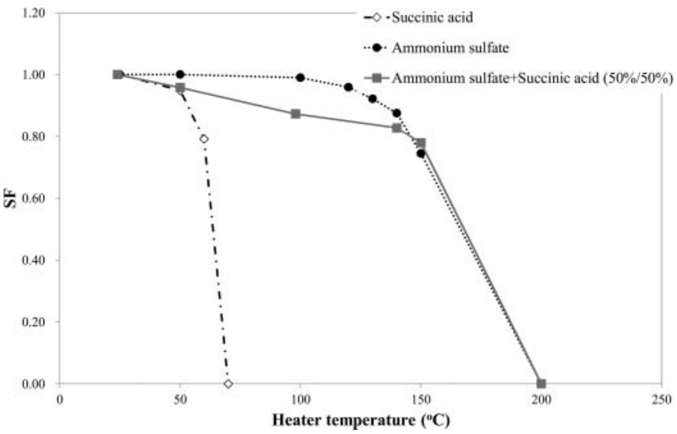

FIG. 10. SFs of size-selected (∼30 nm) succinic acid, ammonium sulfate, and an internal mixture of succinic acid and ammonium sulfate (50%/50%) particles as a function of temperature.

species (i.e., succinic acid) was calculated at 150°C, it was ∼53%, which is close to the expected value from the 50%/50% solution mixture.

## 4. CONCLUSIONS

In this study, an HTDMA system with a thermodenuder was applied to determine the mixing state of size-selected particles in combustion and photochemical events in an urban area of Gwangju, Korea. It was found that in the combustion event, the accumulation mode particles (137–139 nm) increased and had a nonvolatile core, which is consistent with TEM images of the submicrometer particles. When the hygroscopicity of the core particles was measured at a heater temperature of 250°C, the HGF of the particles decreased after removing volatile species, suggesting that the core particles mainly consist of nonvolatile and nonhygroscopic carbonaceous species (e.g., BC) and that the volatile species included some hygroscopic species. In the photochemical event, the nucleation mode particles (15–30 nm) increased and had no nonvolatile core (i.e., they were completely evaporated below 250°C). The nucleation mode particles had some volatile fraction at 100°C unlike pure ammonium sulfate and had C and S elements in their TEM/EDS data, suggesting that they have an internal mixture of sulfate and organics. It was also found that HGFs of the remaining particles after removing volatile species at 150°C increased compared to those of particles before heating, but not as high as expected, due to the existence of less hygroscopic and volatile species at this temperature. Data for laboratory-generated aerosols suggest that the evaporation of volatile species existing in an internal mixture (i.e., "well-mixed" mixture of sulfate and succinic acid) was delayed compared to that of pure species.

## REFERENCES

Adachi, K., and Buseck, P. R. (2008). Internally Mixed Soot, Sulfates, and Organic Matter in Aerosol Particles from Mexico City. *Atmos. Chem. Phys.*, 8:6469–6481.

Adachi, K., Freney, E. J., and Buseck, P. R. (2011). Shapes of Internally Mixed Hygroscopic Aerosol Particles after Deliquescence, and Their Effect on Light Scattering. *Geophys. Res. Lett.*, 38:L13804–L13808, Doi:10.1029/2011GL047540.

Andreae, M. O. (2007). Aerosols Before Pollution. *Science*, 315:50–51.

Andreae, M. O. (2009). A New Look at Aging Aerosols. *Science*, 326: 1493–1494.

Bakand, S., Hayes, A., and Dechsakulthorn, F. (2012). Nanoparticles: A Review of Particle Toxicology Following Inhalation Exposure. *Inhal. Toxicol.*, 24:125–135.

Biskos, G., Russell, L. M., Buseck, P. R., and Martin, S. T. (2006). Nanosize Effect on the Hygroscopic Growth Factor of Aerosol Particles. *Geophys. Res. Lett.*, 33:L07801–L07804. Doi:10.1029/2005GL025199.

Biskos, G., Buseck, P. R., and Martin, S. T., (2009). Hygroscopic Growth of Nucleation-Mode Acidic Sulfate Particles. *J. Aerosol Sci.*, 40(4), 338–347.

Bond, T. C., and Bergstrom, R. W. (2006). Light Absorption by Carbonaceous Particles: An Investigative Review. *Aerosol Sci. Technol.*, 40:27–67.

Chandra, S., Satheesh, S. K., and Srinivasan, J. (2004). Can the State of Mixing of Black Carbon Aerosols Explain the Mystery of 'Excess' Atmospheric Absorption? *Geophys. Res. Lett.*, 31:L19109–L19112. Doi:10.1029/2004GL020662.

Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley, J. A. Jr., Hansen, J. E., and Hofmann, D. J. (1992). Climate Forcing by Anthropogenic Aerosols. *Science*, 255:423–430.

Chen, D. R., Pui, D. Y. H., Hummes, D., Fissan, H., Quant, F. R., and Sem, G. J. (1998). Design and Evaluation of a Nanometer Aerosol Differential Mobility Analyzer (Nano-DMA). *J. Aerosol Sci.*, 29:497–509.

Dey, S., Tripathi, S. N., and Mishra, S. K. (2008). Probable Mixing State of Aerosols in the Indo-Gangetic Basin, Northern India. *Geophys. Res. Lett.*, 35:L03808–L03812. Doi:10.1029/2007GL03 2622.

Dixkens, J., and Fissan, H. (1999). Development of an Electrostatic Precipitator for Off-Line Particle Analysis. *Aerosol Sci. Technol.*, 30:438–453.

Freney, E. J., Adachi, K., and Buseck, P. R. (2010). Internally Mixed Atmospheric Aerosol Particles: Hygroscopic Growth and Light Scattering. *J. Geophy. Res.*, 115:D19210–D19218. Doi:10.1029/2009JD01 3558

Grose, M., Sakurai, H., Savstrom, J., Stolzenburg, M., Watts, W., Morgan, C., Murray, I., Twigg, M., Kittelson, D., and McMurry, P. H. (2006). Chemical and Physical Properties of Ultrafine Diesel Exhaust Particles Sampled Downstream of a Catalytic Trap. *Environ. Sci. Technol.*, 40(17):5502–5507.

Hämeri, K., Charlson, R., and Hansson, H. C. (2002). Hygroscopic Properties of Mixed Ammonium Sulfate and Carboxylic Acids Particles. *AICHE J.*, 48:1309–1316.

IPCC. (2007). *Climate Change*. Cambridge University Press, New York.

Jacobson, M. Z. (2000). A Physically-Based Treatment of Elemental Carbon Optics: Implications for Global Direct Forcing of Aerosols. *Geophys. Res. Lett.*, 27:217–220.

Jacobson, M. Z. (2001). Strong Radiative Heating Due to the Mixing State of Black Carbon in Atmospheric Aerosols. *Nature*, 409:695–697.

Johnson, G. R., Ristovski, Z., and Morawska, L. (2004). Method for Measuring the Hygroscopic Behaviour of Lower Volatility Fractions in an Internally Mixed Aerosol. *J. Aerosol Sci.*, 35:443–455.

Johnson, G. R., Ristovski, Z. D., D'Anna, B., and Morawska, L. (2005). Hygroscopic Behavior of Partially Volatilized Coastal Marine Aerosols Using the Volatilization and Humidification Tandem Differential Mobility Analyzer Technique. *J. Geophys. Res.*, 110:D20203. Doi:10.1029/2004JD005657.

Kanakidou, M., Seinfeld, H. J., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Dingenen, R. V., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J., 2005. Organic Aerosol and Global Climate Modeling: A Review. *Atmos. Chem. Phys.*, 5:1053–1123.

Knutson, E. O., and Whitby, K. T. (1975). Aerosol Classification by Electric Mobility: Apparatus, Theory, and Applications. *J. Aerosol Sci.*, 6:443–451.

Koloutsou-Vakakis, S., Rood, M. J., Nenes, A., and Pilinis, C. (1998). Modeling of Aerosol Properties Related to Direct Climate Forcing. *J. Geophys. Res.*, 103:17009–17032.

Lightstone, J. M., Onasch, T. B., and Imre, D. (2000). Deliquescence, Efflorescence, and Water Activity in Ammonium Nitrate and Mixed Ammonium Nitrate/Succinic Acid Microparticles. *J. Phys. Chem. A.*, 104:9337–9346.

McMurry, P. H., and Stolzenburg, M. R. (1989). On the Sensitivity of Particle Size to Relative Humidity for Los Angeles Aerosols. *Atmos. Environ.* 23(2): 497–507.

Michaud, V., Haddadd, I. E., Liu, Y., Sellegri, K., Laj, P., Vilani, P., Picard, D., Marchand, N., and Monod, A. (2009). In-Cloud Processes of Methacrolein under Simulated Conditions—Part 3: Hygroscopic and Volatility Properties of the Formed Secondary Organic Aerosol. *Atmos. Chem. Phys.* 9(14): 5119–5130.

Mikhailov, E. F., Vlasenko, S. S., Podgorny, I. A., Ramanathan, V., and Corrigan, C. E. (2006). Optical Properties of Soot-Water Drop Agglomerates: An Experimental Study. *J. Geophys. Res.*, 111:D07209. Doi:10.1029/2005JD006389

Moffet, R. C., and Prather, K. A. (2009). In-Situ Measurements of the Mixing State and Optical Properties of Soot with Implications for Radiative Forcing Estimates. *Proc. Natl. Acad. Sci. U.S.A.*, 106:11872–11877.

Park, K., Kim, J. S., and Miller, A. L. (2009a). A study on Effects of Size and Structure on Hygroscopicity of Nanoparticles Using a Tandem Differential Mobility Analyzer and TEM. *J. Nanopart. Res.*, 11:175–183.

Park, K., Kim, J. S., and Park, S. H. (2009b). Measurements of Hygroscopicity and Volatility of Atmospheric Ultrafine Particles During Ultrafine Particle Formation Events at Urban, Industrial, and Coastal Sites. *Environ. Sci. Technol.*, 43:6710–6716.

Park, K., Park, J. Y., Kwak, J. H., Cho, G. N., and Kim, J. S. (2008). Seasonal and Diurnal Variations of Ultrafine Particle Concentration in Urban Gwangju, Korea: Observation of Ultrafine Particle Events. *Atmos. Environ.*, 42:788–799.

Park, S. H., Gong, S. L., Bouchet, V. S., Gong, W., Makar, P. A., Moran, M. D., Stroud, C. A., and Zhang, J. (2011). Effects of Black Carbon Aging on Air Quality Predictions Direct Radiative Forcing Estimation. *Tellus Ser. B: Chem. Phys. Meteorol.*, 63:1026–1039.

Péré, J. C., Mallet, M., Bessagnet, B., and Pont, V. (2009). Evidence of the Aerosol Core-Shell Mixing State Over Europe During the Heat Wave of Summer 2003 by Using CHIMERE Simulations and AERONET Inversions. *Geophys. Res. Lett.*, 36:L09807–L09811. Doi:10.1029/20 09GL037334.

Prenni, A. J., DeMott, P. J., and Kreidenweis, S. M. (2003). Water Uptake of Internally Mixed Particles Containing Ammonium Sulfate and Dicarboxylic Acids. *Atmos. Environ.*, 37:4243–4251.

Rader, D. J., and McMurry, P. H. (1986). Application of the Tandem Differential Mobility Analyzer to Studies of Droplet Growth or Evaporation. *J. Aerosol Sci.*, 17:771–787.

Riemer, N., West, M., Zaveri, R. A., and Easter, R. C. (2009). Simulating the Evolution of Soot Mixing State with a Particle-Resolved Aerosol Model. *J. Geophys. Res.*, 114:D09202. Doi:10.1029/2008JD011073.

Ristovski, Z. D., Suni, T., Kulmala, M., Boy, M., Meyer, N. K., Duplissy, J., Turnipseed, A., Morawska, L., and Baltensperger, U. (2010). The Role of Sulphates and Organic Vapours in Growth of Newly Formed Particles in a Eucalypt Forest. *Atmos. Chem. Phys.*, 10:2919–2926.

Rose, D., Wehner, B., Ketzel, M., Engler, C., Voigtländer, J., Tuch, T., and Wiedensohler, A. (2006). Atmospheric Number Size Distributions of Soot Particles and Estimation of Emission Factors. *Atmos. Chem. Phys.*, 6(4):1021–1031.

Sakurai, H., Tobias, H. J., Park, K., Zarling, D., Docherty, K. S., Kittelson, D. B., McMurry, P. H., and Ziemann, P. J. (2003). On-Line Measurements of Diesel Nanoparticle Composition and Volatility. *Atmos. Environ.* 37(9–10): 1199–1210.

Satheesh, S. K., Krishna Moorthy, K., Suresh Babu, S., Vinoj, V., and Dutt, C. B. S. (2008). Climate Implications of Large Warming by Elevated Aerosol Over India. *Geophys. Res. Lett.*, 35:L19809. Doi:10.1029/2008GL034944.

Satheesh, S. K., Srinivasan, J., Vinoj, V., and Chandra, S. (2006). New Directions: How Representative are Aerosol Radiative Impact Assessments? *Atmos. Environ.*, 40:3008–3010.

Seinfeld, J. H., and Pandis, S. N. (1998). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. Wiley, New York.

Srivastava, R., and Ramachandran, S. (2013). The Mixing State of Aerosols Over the Indo-Gangetic Plain and Its Impact on Radiative Forcing. *Q. J. R. Meteorol. Soc.*, 139:137–151.

Tumolva, L., Park, J. Y., Kim, J. S., Miller, A. L., Chow, J. C., Watson, J. G., and Park, K. (2010). Morphological and Elemental Classification of Freshly Emitted Soot Particles and Atmospheric Ultrafine Particles Using the TEM/EDS. *Aerosol Sci. Technol.*, 44:202–215.

Villani, P., Picard, D., Michaud, V., Laj, P., and Wiedensohler, A. (2008). Design and Validation of a Volatility Hygroscopic Tandem Differential Mobility Analyzer (VH-TDMA) to Characterize the Relationships Between the Thermal and Hygroscopic Properties of Atmospheric Aerosol Particles. *Aerosol Sci. Technol.*, 42:729–741.

Wise, M. E., Surratt, J. D., Curtis, D. B., Shilling, J. E., and Tolbert, M. A. (2003). Hygroscopic Growth of Ammonium Sulfate/Dicarboxylic Acids. *J. Geophys. Res.*, 108:D204638. Doi:10.1029/2003JD003775.

Xue, H., Khalizov, A. F., Wang, L., Zheng, J., and Zhang, R. (2009). Effects of Coating of Dicarboxylic Acids on the Mass-Mobility Relationship of Soot Particles. *Environ. Sci. Technol.*, 43:2787–2792.

Zhang, X. Q., McMurry, P. H., Hering, S. V., and Casuccio, G. S. (1993). Mixing Characteristics and Water Content of Submicron Aerosols Measured in Los Angeles and at the Grand Canyon. *Atmos. Environ.*, 27A:1593–1607.

Zhang, R., Khalizov, A. F., Pagels, J., Zhang, D., Xue, H., and McMurry, P. H. (2008). Variability in Morphology, Hygroscopicity, and Optical Properties of Soot Aerosols During Atmospheric Processing. *Proc. Natl. Acad. Sci. U.S.A.*, 105:10291–10296.

Zimmermann, R. (2011). Ambient Aerosols and Human Health: Working Towards a Combined Analytical and Toxicological Approach. *Anal. Bioanal. Chem.*, 401:3041–3044.