https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Atmospheric Measurement Techniques Discussions
Open Access
EGU

Nano-hygroscopicity tandem differential mobility analyzer (nano-HTDMA) for investigating hygroscopic properties of sub-10 nm aerosol nanoparticles

Ting Lei[1,2], Nan Ma[4,1,3], Juan Hong[4,1], Thomas Tuch[3], Xin Wang[2], Zhibin Wang[5], Mira Pöhlker[2], Maofa Ge[6], Weigang Wang[6], Eugene Mikhailov[7], Thorsten Hoffmann[8], Ulrich Pöschl[2], Hang Su[2], Alfred Wiedensohler[3], Yafang Cheng[1]

[1]Minerva Research Group, Max Planck Institute for Chemistry, 55128 Mainz, Germany

[2]Multiphase Chemistry Department, Max Planck Institute for Chemistry, 55128 Mainz, Germany

[3]Leibniz Institute for Tropospheric Research, 04318 Leipzig, Germany

[4]Institute for Environmental and Climate Research, Jinan University, 511443 Guangzhou, China

[5]Reserch Center for Air Pollution and Health, College of Environmental and Resource Science, Zhejiang University, Hangzhou, 310058, China

[6]Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China

[7]St. Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034, Russia

[8]Institute of Inorganic Chemistry and Analytical Chemistry, Johannes Gutenberg University Mainz, Mainz, Germany

Correspondence to: Yafang Cheng (yafang.cheng@mpic.de) and Juan Hong (juanhong0108@jnu.edu.cn)

Abstract. Interactions between water and nanoparticles are relevant for atmospheric multiphase processes, physical chemistry, and materials science. Current knowledge of the hygroscopic and related physico-chemical properties of nanoparticles, however, is restricted by limitations of the available measurement techniques. Here, we present the design and performance of a nano-hygroscopicity tandem differential mobility analyzer (nano-HTDMA) apparatus that enables high accuracy and precision in hygroscopic growth measurements of aerosol nanoparticles with diameters less than 10 nm. Detailed methods of calibration and validation are provided. Beside maintaining accurate and stable sheath/aerosol flow rates (±1%), high accuracy of DMA voltage (±0.1%) in the range of ~0-50 V is crucial to achieve accurate sizing and small sizing offsets between the two DMAs (<1.4%). To maintain a stable relative humidity (RH), the

humidification system and the second DMA are placed in a well-insulated and air conditioner housing (±0.1K). We also tested and discussed different ways of preventing pre-deliquescence in the second DMA. Our measurement results for ammonium sulfate nanoparticles are in good agreement with Biskos et al. (2006b), with no significant size-effect on the deliquescence and efflorescence relative humidity (DRH, ERH) at diameters down to 6 nm. For sodium sulfate nanoparticles, however, we find a pronounced size-dependence of DRH and ERH between 20 and 6 nm nanoparticles.

1 Introduction

The climatic effects of aerosol nanoparticles have attracted increasing interests in recent years (Wang et al., 2016; Andreae et al., 2018; Fan et al., 2018). Aerosol nanoparticles in the atmosphere are mostly originating from new particle formation, and a fraction of these nanoparticles could potentially grow into sizes to efficiently act as cloud condensation nuclei and thus to change the contributions of aerosol nanoparticles to climate forcing (Lihavainen 2003; Wiedensohler et al., 2009; Sihto et al., 2011; Kirkby et al., 2011; Keskinen et al., 2013; Dunne et al., 2016; Kim et al., 2016). These processes strongly depend on the chemical composition and physico-chemical properties of these nanoparticles (Köhler, 1936; Su et al., 2010; Wang et al., 2015; Cheng et al., 2015). One of the most important physico-chemical properties of nanoparticles is their hygroscopic behavior that describes their ability to take up water, and it can differ significantly from that of larger particles (Hämeri et al., 2000, 2001; Gao et al., 2006; Biskos et al., 2006a, b, 2007; Cheng et al., 2015).

To understand and predict hygroscopic properties of nanoparticles, current thermodynamic models mostly rely on the concentration-dependent thermodynamic properties (such as water activity and interfacial energy) derived from the measurements of large aerosol particles or even bulk samples (Tang and Munkelwitz, 1994; Tang 1996; Pruppacher and Klett, 1997; Clegg et al., 1998). They are thus difficult or impossible to be applied to describe the hygroscopic behavior of sub-10 nm particles which can be often

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

supersaturated in concentration compared to bulk solutions (Cheng et al., 2015). Furthermore, the nanosize effect on these properties may also need to be considered (Cheng et al., 2015). The lack of such data hinders the understanding and an accurate simulation of the interaction of water vapor and atmospheric nanoparticles. In addition, by knowing the hygroscopicity of newly formed nanoparticle, one can infer the involving chemical species (e.g., organic ratio) in particle formation and initial growth (Wang et al., 2010), which is otherwise difficult and highly challenge to measure directly (Wang et al., 2010; Ehn et al., 2014). Hence, to measure the hygroscopicity of nanoparticles is essential to improve our understandings of aerosol formation, transformation, and their climate effects.

Different techniques have been employed to characterize the hygroscopic properties of aerosol particles in different sizes (Fig. S1) (Tang et al., 2019), such as Fourier transform infrared spectrometer (FT-IR) (Zhao et al., 2006), Raman spectroscopy (Dong et al, 2009), electrodynamic balance (EDB) (Chan and Chan, 2003, 2005; Chan et al., 2008), optical tweezers (Reid et al., 2011; Rickards et al., 2013), hygroscopicity tandem differential mobility analyzer (HTDMA) (e.g., Rader and McMurry, 1986; Mikhailov et al., 2004; 2008; 2009; Biskos et al., 2006a, b, 2007; Cheng et al., 2008, 2009; Eichler et al., 2008; Stock et al., 2011; Hong et al., 2014, 2015; Lei et al., 2014; 2018; Mikhailov and Vlasenko, 2019), and atomic force microscopy (AFM) (Estillore et al., 2017). Using these techniques, most of the early lab studies focuses on the hygroscopic behavior of particles in accumulation modes and super-micron size range, including deliquescence, efflorescence of pure components and the effect of organics on the change or suppression of deliquescence and efflorescence of these inorganic components in mixtures.

For nanoparticles with diameters down to sub-10 nm, there are, however, only very few studies attempting to investigate their interactions with water molecules, which mainly utilized the setup with humidified tandem DMAs (Hämeri et al., 2000, 2001; Sakurai et al., 2005; Biskos et al., 2006a, b, 2007; Giamarelou et al., 2018). In Table S1, we summarized the measured DRH and ERH of ammonium sulfate nanoparticles in the size range from 6 to 100 nm using HTDMAs. In these studies, the results of the observed

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

deliquescence and efflorescence relative humidity (respective DRH and ERH) and prompt or non-prompt phase transitions of ammonium sulfate nanoparticles, however, do not show universal agreement. The technical challenges in HTDMA measurements, especially in the sub-10 nm size range, mainly lie on: (1) accurate sizing and small sizing offset of the two DMAs, (2) highly stable measurement conditions in the whole system. Large sizing offset between the two DMAs may lead to significant error in the measured growth factor based on error propagation (Mochida and Kawamura, 2004). Massling et al. (2011) and Zhang et al. (2016) suggested that to achieve good hygroscopic growth factor of nanoparticles, the sizing offset of the two DMAs should be within ±2-3%, which is however very difficult to maintain for the sub-10 nm size range. To accurately measure phase transition (e.g., DRH and ERH), a highly stable measurement condition is essential, especially maintaining a small temperature perturbation in the humidification system and inside the second DMA to prevent pre-deliquesce. For example, a 0.8 K fluctuation of the experimental temperature during the measurement can result in a 4% difference in RH (0-90%) inside the humidified DMA (Hämeri et al., 2000), leading to an inaccurate determination of the phase transition. Another problem is the prompt versus non-prompt phase transition. Although effects of impurities on the phase transition of aerosol nanoparticles (Biskos et al., 2006a; Russell and Ming, 2002) may be one possible reason of the previously observed non-prompt phase transitions (e.g., Hämeri et al., 2000), the apparent non-prompt phase transition of aerosol nanoparticles has been thought to be mainly due to the inhomogeneity of RH and temperature in the humidified DMA during measurements (Biskos et al., 2006b; Bezantakos et al., 2016). Moreover, the hygroscopic measurements are in general difficult for nanoparticles with diameters below 20 nm due to high diffusion losses of nanoparticles (Seinfeld and Pandis, 2006).

In this study, we present a design of nano-HTDMA setup that enables high accuracy and precision in hygroscopic growth measurements of aerosol nanoparticles with diameters less than 10 nm. Detailed methods of calibration and validation are provided. We discuss in detail how to maintain the good performance of the system by minimizing uncertainties associated with the stability and accuracy of RH,

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

temperature, voltage for nanoparticle classification, and sheath and aerosol flows in the DMA systems. We then apply the nano-HTDMA system to study the size dependence of the deliquescence and the efflorescence of aerosol nanoparticles of two specific inorganic compounds (e.g., ammonium sulfate and sodium sulfate) for sizes down to 6 nm.

2. Methods

2.1 Nano-HTDMA system

A nano-HTDMA system is built up to measure the aerosol nanoparticle hygroscopic growth factor (g_f), especially aiming for accurate measurement of phase transition and hygroscopic growth factor for nanoparticles in the sub-10 nm size range. Here, g_f is defined as the ratio of mobility diameters of nanoparticles after humidification ($D_m(RH)$) to that at dry condition (D_m(< 10% RH)) (see SI. Eq. (S1)). As presented in Fig. 1, the nano-HTDMA composes three main components, including two nano-differential mobility analyzers (nano-DMA, TROPOS Model Vienna-type short DMA; Birmili et al., 1997), an ultrafine condensation particle counter (CPC, TSI Model 3776), and a humidification system. Table 1 shows the technical specification, where the DMA system, humidification system, and temperature system of the three HTDMAs setup are compared among the systems of Biskos et al. (2006b), Hämeri et al. (2000) and this study.

In our setup (Fig. 1), the first nano-DMA (nano-DMA1) is used to produce quasi-monodisperse nanoparticles at a desired dry diameter. The flow rate of the closed-loop sheath flow in the nano-DMA1 is maintained at 10 l/min. The ratio of sheath flow to aerosol flow is 10:1.5. The sheath flow is dried to RH below 10% by two custom-built Nafion dryers (TROPOS Model ND.070) in parallel. The quasi-monodisperse nanoparticles produced by nano-DMA1 then enter the humidification system, which can be set to deliquescence mode (from low RH to high RH for measuring deliquescence) or efflorescence mode (from high RH to low RH for measuring efflorescence). In the deliquescence mode, dry nanoparticles are humidified by a Nafion humidifier (NH-1, TROPOS Model ND.070, L. 24″) to a target RH. In the efflorescence mode, nanoparticles are first exposed to a high RH condition (~97% RH) in a Nafion humidifier (NH-2, Perma Pure Model MH-110, L. 12″) and then dried to a target RH through NH-1. The humid flow in the outer tube of NH-1 is a mixture of high-humidity air produced with a custom-built Gore-Tex humidifier and heater (GTHH: TROPOS Model Di. 0.6″, L. 11.8″) and dry air in variable proportions. To have a precise control of the aerosol RH, the flow rates of the humid and dry air are adjusted with a proportional-integral-derivative (PID) system, including two mass flow controllers (MFC: MKS Model MF1) and a RH sensor (Vaisala Model HMT330) downstream of NH-1.

The residence time is ~5.4 s in the NH-1for both the deliquescence and the efflorescence mode. Many groups have reported that the residence time of a few seconds is sufficient to reach equilibrium for measuring hygroscopic growth or shrink of inorganic salts particles, e.g., ammonium sulfate and chloride sodium (Chan and Chan, 2005; Duplissy et al., 2009; Lei et al., 2014, 2018; Giamarelou et al., 2018). More specifically, Kerminen (1997) estimated the time for reaching the water equilibrium to be between 8 x 10^{-6} s and 0.005 s for 100 nm nanoparticles at 90% RH at 25°C with accommodation coefficients from 0.001 to 1, respectively. In our study, we measured the inorganic aerosol nanoparticles with diameters from ~100 nm down to 6 nm, thus the equilibrium time should be even shorter as nanoparticle size decreases (Table. S2). In NH-2, the residence time is ~0.07 s for the deliquescence of inorganic aerosol nanoparticles at very high RH condition (~97% RH), which is much longer than the time estimated for phase transition by Duplissy et al. (2009) (in the order of a few milliseconds) and Raoux et al. (2007) (in the order of a few nanoseconds). In addition, we have tested a longer NH-2 (Perma Pure Model MH-110, L. 48″) in the efflorescence mode, and no significant difference in measured growth factors are found, indicating that the residence time in NH-1 and NH-2 should be sufficient.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

The number size distribution of the humidified nanoparticles is measured with a combination of the second nano-DMA (nano-DMA2) and the ultrafine CPC. Similar to Biskos et al. (2016b), a multiple Nafion humidifier (NH-3, Pure Model PD-100) is used in our nano-HTDMA system to rapidly adjust the RH of the sheath flow of nano-DMA2. The sheath flow is fed into the outer tube of NH-3 to minimize its pressure drop. The RH of humid flow in the inner tube of NH-3 is controlled with a similar PID system as that for NH-1. A RH sensor (Vaisala Model HMT330) downstream of NH-3 is used to provide feedback to the PID system. In our nano-HTDMA system, a dew point mirror (DPM: EDGE TECH Model MIRROR-99) is placed in the excess flow line to measure the RH and temperature of excess flow of the nano-DMA2. During the operation, the difference between sheath flow RH and aerosol flow RH has been maintained within ±1% (see more details in Section 2.2).

The sheath flow is maintained to the set flow rate with a PID-controlled recirculation blower (RB: AMETEK Series MINISPIRAL). Prior to every size scan, the sheath flow rate of nano-DMA2 is adjusted by the PID system according to the measurement of a mass flow meter (MFM: TSI Series 4000) in the sheath flow line. In order to minimize the pressure drop along the recirculating sheath flow loop, low flow resistance MFM and hydrophobic filter (HF: Whatman Model 6702-3600) are used. A heat exchanger (HE, Ebmpapst Model 4414FM) is installed downstream of the RB to minimize the temperature perturbation in the sheath flow by the heat generated in the RB.

As aforementioned, temperature non-uniformity is the main contributor to the fluctuation of RH within humidified DMA. Temperature difference within nano-DMA2 is unavoidable mainly due to temperature difference between inner electrode and the rest of nano-DMA2 parts and/or the temperature difference between aerosol and sheath flow (Duplissy et al., 2009; Bezantakos et al., 2016). As shown in Fig. 1, to investigate and monitor the temperature difference within nano-DMA2 during measurements, a temperature sensor (THERMO ELECTRON Model Pt100) is placed at the inlet of the sheath flow and the temperature of sheath excess flow is monitored by the DPM. Note that, a DPM should be installed as close

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

as possible to the nano-DMA2 in the excess flow, which better represents the conditions inside the nano-DMA2, such as temperature and RH (Wiedensohler et al., 2012). In addition, the temperature of aerosol flow is monitored at the inlet of the aerosol flow of nano-DMA2.

Moreover, to maintain a stable environment that required for the growth factor measurements, nano-DMA2 with its sheath flow humidification system is placed in a well-insulated housing chamber (marked with yellow dashed lines in Fig. 1). An air conditioner (Telemeter Electro Model TEK-1004-RR-24-IP55) is installed inside the housing to maintain a constant temperature (292.15±0.1 K), which is set to be ~1 K lower than the constant laboratory temperature (293 K) in order to achieve high RH (~90%) inside nano-DMA2.

2.2 Calibration of nano-HTDMA

The purpose of this study is to design and build a nano-HTDMA system that is able to measure the hygroscopic properties of nanoparticles, especially in the sub-10 nm size range. A small perturbation in the measurement conditions may lead to large biases in the results. Hence, to provide high quality hygroscopicity measurements of nanoparticles, systematic calibration of the nano-HTDMA should be conducted regularly to ensure the accuracy and stability of the measurement conditions. Table 1 lists the possible sources of uncertainty, which could affect the performance of the HTDMAs. In our setup, nanoparticle sizing, aerosol/sheath flow rates, the high voltage (HV) applied to nano-DMAs, RH sensors, and temperature sensors are calibrated and verified independently.

Note that in the following, for calibration and/or checking of different parameters, the criteria and/or standard that the nano-HTDMA system has to meet are listed mainly according to the suggestions from Duplissy et al., (2009) and Wiedensohler et al. (2012), which are not specifically provided for accurately measuring sizes or hygroscopic growth of sub-10 nm nanoparticles. Compared with these criteria, to measure hygroscopic growth of sub-10 nm nanoparticles, we have achieved a better condition for our nano-

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

HTDMA system after comprehensive calibrations described as follows (more details about performance of our system see section 3).

2.2.1 Sizing accuracy

For particle diameters higher than 100 nm, the verification of sizing accuracy of DMAs can be accomplished by using certified particles of known sizes such as polystyrene latex (PSL) spheres (Hennig et al., 2005; Mulholland et al., 2006; Duplissy et al., 2009; Wiedensohler et al., 2012, 2018). The particle sizing of nano-DMA2 is checked with PSL by switching off the sheath flow and the HV supply of nano-DMA1, which actually in this case does not function as a DMA, but rather a stainless-steel tube. Sizing agreement between measured diameters and nominal diameters of PSL particles above 100 nm should be within ±3% (Wiedensohler et al., 2012). After confirming the accurate sizing of nano-DMA2, the sizing accuracy of nano-DMA1 can be in turn checked by the nano-DMA2 with a full scan of a certain size of PSL selected by the nano-DMA1. Note that, it is important to check not only the sizing accuracy of both DMAs, but also the sizing agreement between the nano-DMA1 and nano-DMA2. To achieve good hygroscopcity measurements of nanoparticles, the sizing offset of the two DMAs should be within ±2-3% (Massling et al., 2011; Zhang et al., 2016).

For nanoparticles with diameters smaller than 100 nm, the sizing accuracy is, however, difficult to check by using PSL nanoparticles. This is mainly because the size of residual material in the solution also peaks around 20 – 30 nm (Fig. S2a), resulting in an asymmetric number size distribution of generated PSL nanoparticles (Fig. S2b) (Wiedensohler et al., 2012). PSL nanoparticles with diameters below 20 nm are not commercially available (https://www.thermofisher.com/order/catalog/product/3020A), making the verification in this size range even impossible. Sizing accuracy of nanoparticles is critically determined by sheath flow rates and HV applied to the nano-DMAs. However, unlike for the 100 nm nanoparticles, a ±2-3% sizing offset between the two DMAs would be very difficult to maintain for nanoparticles with diameters smaller than 20 nm. Thence, accurate calibrations of sheath flow rates and high voltage are crucial

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

for constraining the uncertainty associated with sizing of nanoparticles below 100 nm. The calibrations for aerosol/sheath flow, DMA voltage, and sensors will be described in detail in the following Section 2.2.2-2.2.5.

2.2.2 Aerosol and sheath flow

Sizing accuracy of a DMA directly depends on the accuracies of aerosol and sheath flow rates. The aerosol flow rate at the inlet of the nano-DMA1 is checked by using a bubble flow meter (Gilian Model Gilibrator-2). Wiedensohler et al. (2012) recommended that the measured aerosol flow rate should not deviate more than 5% from the set flow rate during the measurements, otherwise one should check the flow rate of CPC or if there is a leakage in the system. Details about leakage checking can be found in Birmili et al. (2016).

To calibrate the sheath flow, a verified MFM (TSI Series 4000) is placed in the recirculating sheath flow close-loop upstream of the MFM. By applying a series of sheath flow rates, a calibration curve (flow rate vs. MFM analogue output) can be obtained according to the reading of the reference MFM. Maximum deviation of 2% from the sheath flow rate value of the reference MFM is recommended by Wiedensohler et al. (2012), which can keep sizing accuracy of 200 nm PSL particles within ±2%.

2.2.3 DMA voltage

The sizing of nano-DMAs is very sensitive to the accuracy and precision of the voltages applied, especially when measuring nanoparticles in the sub-10 nm diameter range. A verified reference voltage meter with voltage up to 1000 V (Prema Model 5000 DMM, accuracy 0.005%) is used to calibrate the HV supply of the nano-DMAs (0-350 V). By setting a series of analogue voltage values, the HV applied to nano-DMA can be calibrated according to the values shown in the reference voltage meter. For our nano-DMAs, sub-10 nm in particle sizes correspond to voltage below 50 V. Thence, voltage calibration should be performed with a higher resolution (smaller voltage interval) from 0 to 50 V (shown in the insert of Fig. 2).

2.2.4 RH sensor

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

One typical method to calibrate RH sensors in a HTDMA system is to measure the hygroscopic growth factors of ammonium sulfate (Hennig et al., 2005), although the effects of shape factors, restructuring, and impurities in the solutions may hamper a reliable RH calibration with this method (Duplissy et al., 2009). Moreover, this indirect RH sensor calibration through measurement of the hygroscopic growth factors of ammonium sulfate (usually with nanoparticle diameters around or above 100 nm) only calibrates the RH values higher than the ERH of the pure salt. Calibration of RHs below ERH of ammonium sulfate is important for the phase transition measurements. Most importantly, we are investigating the hygroscopic growth factors of ammonium sulfate nanoparticles. Hence, using ammonium sulfate nanoparticles to calibrate RH sensors in our system becomes invalid.

Therefore, we alternatively calibrate the RH sensors by using a DPM (EDGE TECH Model MIRROR-99), which is recommended in several previous studies (Hennig et al., 2005; Duplissy et al., 2009; Biskos et al., 2006a, b, 2007). In the calibration, the DPM and RH sensors should be kept in the well-insulated chamber with constant laboratory conditions (e.g., flow rates, temperature, and pressure). By running the DPM and all the other RH sensors in parallel at various RHs (5% to 90%), a calibration curve of the RHs measured by the DPM against analogue voltages of RH sensor can be obtained.

2.2.5 Temperature sensor

Since all our temperature sensors and the high accurate DPM (EDGE TECH Model MIRROR-99) are installed in the aforementioned well-insulated chamber and the chamber temperature is maintained with air conditioner at about 292.15±0.1 K, we calibrate the temperature sensors and corrected their systematic shift by comparing the record of temperature sensors and the DPM by keeping them in parallel inside the chamber over a 12-hour time period.

2.3 Particle generation

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

The experiments shown in this study were conducted using laboratory generated ammonium sulfate and sodium sulfate nanoparticles. Nanoparticles with diameters of 6, 8, and 10 nm were generated by an electrospray (AG: TSI Model 3480) with 1, 5, and 20 mM aqueous solution of ammonium sulfate and sodium sulfate (Aldrich, 99.99%), respectively. The generated particles were then diluted and dried to RH below 2% by mixing with dry and filtered N_2 (1 l/min) and CO_2 (0.1 l/min). The dried polydisperse aerosol nanoparticles were subsequently neutralized by a Po^{210} neutralizer. To avoid blocking the 25-μm capillary of the electrospray with high solution concentration, we used an atomizer (AG: TSI Model 3076) to generate nanoparticles with diameters of 60-100 nm and 20nm with 0.05 and 0.001 wt% solution of ammonium sulfate and sodium sulfate (Aldrich, 99.99%), respectively. Also, 100-nm PSL nanoparticles were atomizing a PSL solution of mixing 3 drops of 100-nm PSL with 300 mL distilled and de-ionized milli-Q water. The generated nanoparticles were subsequently dried to RH below 10% with a custom-built Nafion dryer (ND: TROPOS Model ND.070) and then neutralized by a Kr^{85} neutralizer.

The solutions used in our measurements were prepared with distilled and de-ionized milli-Q water (resistivity of 18.2 MΩ cm at 298.15 K). Note that, for 100-60 nm and 20 nm, the solution concentration was adjusted so that the sizes selected by the nano-DMA1 were always larger than the peak diameter of the number size distribution of the generated nanoparticles to minimize the influence of the multiple charged nanoparticles in hygroscopicity measurements. The influence of multiple charges on sub-10 nm particles is expected to be very small, we, however, still used different concentrations so that the sizes selected by the nano-DMA1 were always around the peak of the number size distribution of the generated nanoparticles by the electrospray (Fig. S3). This is to ensure that we could have as many particles as possible to compensate the strong loss of very small particles in the whole humidification systems.

3 Results and discussion

3.1 Performance of the nano-HTDMA

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

3.1.1 Sizing accuracy

In this section, we show the performance of our nano-HTDMA after a full calibration, including accuracy and stability of the aerosol/sheath flow rates, the voltage applied to the nano-DMAs, and nanoparticle-sizing accuracy. In our study, the sheath/aerosol flow rates and nano-DMA voltage supply have been calibrated every day and every two weeks, respectively. The deviations of the measured aerosol/sheath flow rates from the set-point values are less than ±1%, which is lower than the maximum variation of 2% recommended by Wiedensohler et al. (2012).

The voltage applied to the nano-DMAs (up to 350 V) is kept within ±0.1% around the set value shown in the voltage meter. As shown in Fig. 3a, when test with 100-nm PSL nanoparticles, the average peak diameter of scans from the nano-DMA2 is 100.4 nm, which matches well with the mean diameter of PSL nanoparticles (100±3 nm, Thermo Fisher Scientific Inc.). Afterwards, when using nano-DMA1 select 100 nm PSL, the scanned size distribution by nano-DMA2 has a peak diameter at 100.3 nm (Fig. 3b), indicating a good sizing accuracy of the nano-DMA1 too.

After calibration, on average a <1.4% sizing offset between the two nano-DMAs can be achieved for ammonium sulfate nanoparticles with dry diameters of 100 nm, 60 nm and 20 nm (Fig. 3c, Fig.5, Table S3, Fig. S4, and Fig. S5), which is much better than the 2-3% criteria recommended by Massling et al. (2011) and Zhang et al. (2016). For sub-10 nm ammonium sulfate nanoparticles, our system has an average sizing offset of <0.9% for 10 and 8 nm particles and ~1.4% for 6 nm particles, respectively (Fig. 3d, Fig. 5, Table S3, and Fig. S6). Note that, we also tested to calibrate the DMA voltage with a voltage meter with lower accuracy of ±1%, and the DMA voltages can only be kept within ±1% around the set value. In this way, we found a much larger sizing offset for the sub-10 nm particles, i.e., 5.4% and 6.0% for 8 and 6 nm ammonium sulfate nanoparticles, respectively. These results show that maintaining an accurate sheath/aerosol flow (with ±1% around the set value) together with a careful voltage calibration (with ±0.1%

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Atmospheric Measurement Techniques Discussions

around the set value, especially in low voltage range, i.e., <50 V for our system) is the key for accurate sizing of sub-10 nm nanoparticles.

3.1.2 Preventing pre-deliquescence in the deliquescence measurement mode

Pre-deliquescence of dry nanoparticles in the deliquescence measurement mode is an important issue that needs to be resolved in order to obtain accurate DRH (Biskos et al., 2006b; Duplissy et al., 2009; Bezantakos et al., 2016; Hämeri et al., 2000). Since temperature and RH are closely linked and accurate monitoring of these two quantities in the system are critical for nano-HTDMA measurements, we calibrated all RH and T sensors regularly (every two weeks in this study). To prevent pre-deliquescence and optimize the system, we have conducted three tests using ammonium sulfate nanoparticles with a dry diameter of 100 nm. In the first test, we regulated the RH of excess flow (RH_e) and made it equal to that of the aerosol flow at the inlet of nano-DMA2 (RH_a), i.e., RH_e=RH_a, as done by previous HTDMA measurements, e.g., Villani et al. (2008). As shown in Fig. 4a, the measured growth factors of 100-nm ammonium sulfate are in good agreement with predictions of the Extended Aerosol Inorganic Model (E-AIM; Clegg et al., 1998) at RH above 80%. However, the ammonium sulfate nanoparticles deliquesce at 75% RH, which is significantly lower than the expected DRH (80%, Tang and Munkelwitz (1994)). Since our RH sensors were all well calibrated and the uncertainty of RH measurement is ±1%, it is reasonable to hypothesize that the RH upstream of nano-DMA2 has already reached the deliquesce RH of ammonium sulfate nanoparticles. When these aerosol nanoparticles move downstream of the nano-DMA2, the RH decreases back to 75%, which dehydrate the deliquesced ammonium sulfate nanoparticles. To avoid the pre-deliquescence, Hämeri et al. (2001) has suggested to set RH_a to be 3-5% lower than RH_e. In the second test, we have configured and regulated the system following this suggestion, i.e., $RH_e \geq RH_a$+3%. In this case, the ammonium sulfate nanoparticles still deliquesce at 79% RH (Fig. 4b), even if RH_a is 6% lower than RH_e.

Previous studies (Biskos et al., 2006b; Bezantakos et al., 2016) have shown that RH non-uniformities within the nano-DMA2 can result in inaccurate measurements of phase transition and hygroscopic growth of aerosol nanoparticles. One reason for RH non-uniformities within nano-DMA2 is that the sheath flow RH is different from the aerosol flow RH at the inlet of the DMA (Hämeri et al., 2000, 2001). Another important reason is the existence of temperature gradient within nano-DMA2 (Bezantakos et al., 2016). Hence, in the third test, we moved the RH sensor from the excess flow downstream of nano-DMA2 to the sheath flow upstream of nano-DMA2 and then regulated RH of sheath flow (RH_s) the same as RH_a (shown in Fig. 1), i.e., $RH_s=RH_a$, as done by Kreidenweis et al. (2005), Biskos et al. (2006a, b)., and Massling et al. (2011). Note that to minimize the temperature gradient within the nano-DMA2 in our system so that nanoparticles can undergo almost the same RH conditions, the nano-DMA2 with its sheath flow humidification system has been placed in a well-insulated air-conditioned chamber. The air temperature inside the chamber can be maintained at an almost constant level (292.15±0.1 K). In addition, a heat exchanger was installed downstream of the recirculation blower to minimize the temperature perturbation in the sheath flow by the heat generated in the RB. Unlike previously reported by Bezantakos et al. (2016) that the RH at the outlet was higher than that the inlet of the sheath air, we monitored that the sheath flow temperature at the inlet of nano-DMA2 is slightly lower (less than ~0.2 K) than that at the outlet, i.e., the RH_s at the inlet of nano-DMA2 is slightly higher (~ 1%) than the RH of the excuses air at the outlet. It may due to the heat produced from the inner electrode of nano-DMA2, which we estimated to be ~0.08 W ($Q = mdTC_{p,k}$) by considering the density and heating capacity of air, and aerosol and sheath air flow rate ((ρ=1.2041kg/m^3; C_p= 1.859kJ/kg°C; https://en.wikipedia.org/wiki/Density_of_air; https://www.engineeringtoolbox.com/water-vapor-d_979.html). Although this temperature perturbation (less than ~0.2 K between the sheath flow at the inlet and the excess flow at the outlet of the nano-DMA2) is larger than the ideal condition of less than 0.1 K that Duplissy et al. (2009) and Wiedensohler et al. (2012) suggested, our experimental results show that a prompt phase transition can be still achieved. In this case, the measured DRH of ammonium sulfate nanoparticles is almost at 80% (Fig. 4c and 4d).

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

3.1.3 Prompt phase transition of ammonium sulfate

Figure 5 and 6 show the normalized particle number size distributions measured by the nano-DMA2 in the respective deliquescence and efflorescence measurement modes for ammonium sulfate nanoparticles with dry mobility diameters of 20 nm, 10 nm, and 6 nm (see Fig. S4 for 100 nm, see Fig. S5 for 60 nm, see Fig. S6 for 8 nm). In the deliquescence measurement mode (Fig. 5, Fig. S4a, and Fig. S5a), we observed the similar double-mode phenomenon as reported by Mikhailov et al. (2004) and Biskos et al. (2006b, 2007). For example, at 20 nm, there are two distinct intersecting modes of particle size distributions determined by the nano-DMA2 in the RH range from 79% to 83% RH (around the DRH of ammonium sulfate). Biskos et al. (2006b, 2007) attributed these two modes to the co-existence of solid and liquid phase nanoparticles at RH close to the DRH of ammonium sulfate, due to the slight inhomogeneity of RH in the second nano-DMA, i.e., some nanoparticles have already undergo deliquescence (liquid state) and some are not (solid). This is evident through a double-mode log-normal fitting (red and blue modes in Fig. 5). Until RH ~82%, the peak diameter of the red mode at 82% RH is similar to that at 11% RH, indicating that these nanoparticles are still in a solid state. At 82% RH, a population of ammonium sulfate nanoparticles starts to deliquesce and exists in a distinct mode with significant larger peak diameter (blue mode), although majority of the nanoparticles remain solid (red mode). Further increase RH, the peak diameter of normalized number size distribution of the blue mode increases, indicating the continuous growth the nanoparticles after deliquescence. However, in our case the double-mode phenomenon was not observed for 8 and 6 nm ammonium sulfate nanoparticles (Fig. 5 and Fig. S6a). To have a better estimation of DRH when the double modes occurred, the peak diameter of the mode with larger number of nanoparticles was chosen for growth factor calculation (Biskos et al., 2006b, 2007). For example, for 20 nm ammonium sulfate nanoparticles, the peak diameters of normalized number size distribution of the red and blue modes are used to calculate growth factor at RH between 79% to 83%, respectively.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

For the efflorescence measurement mode, we adopted the approach of Biskos et al. (2006b) and used the geometric standard deviation of number size distribution (sigma: σ) to quantify the diversity of the sizes of nanoparticles. As shown in Fig. 6, Fig. S4b, Fig. S5b, and Fig. S6b, broadening of the normalized number size distributions measured with nano-DMA2 was only observed for 20 nm ammonium sulfate nanoparticles in the RH range from 33% to 30%. There, at RH higher than 33% or lower than 30%, σ stays stably at 1.072. However, clear increases of σ (1.078-1.087) were observed for RH between 33% and 30%. The normalized number size distributions in the RH range from 33% to 30% can be further resolved by double-mode fit with fixed σ of 1.072 (the red and the blue mode in Fig. 6 for 20 nm). The ammonium sulfate nanoparticles in the red mode at RH between 33% to 30% are in solid state because the peak diameter of red mode is similar as that at 11% RH. However, within this RH range, the peak diameter of the blue mode is significantly larger, indicating that these nanoparticles are still in liquid state. Further decreasing RH (lower than 30%), only one mode has been observed and the peak diameter of the normalized number size distribution almost unchanged as RH decreases (red mode in Fig. 6 for 20nm), which means that the nanoparticles have been all in the solid state. Similar to the deliquescence measurement shown above and in Fig. 5, the co-existence of solid and aqueous phase nanoparticles at RH 30-33% is also very likely to stem from the slight heterogeneous RH in nano-DMA2 (Biskos et al., 2006b). To have a better estimation of ERH when the broadening phenomenon exists, the peak diameter of the mode with larger number of nanoparticles was used for growth factor calculation. After such data processing in both deliquescence and efflorescence modes, we obtained prompt deliquescence and efflorescence of 6 to 100 nm ammonium sulfate nanoparticles (more details in Section 3.1.4).

3.1.4 Size-dependent hygroscopicity of ammonium sulfate nanoparticles

Figure 7 shows the humidogram of ammonium sulfate nanoparticles measured by our nano-HTDMA system in the size (dry diameter) range of 6-100 nm. The detailed comparison between our results and Biskos et al. (2006b) during both deliquescence and efflorescence measurements are presented in Fig. 8a

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

and b (also Fig. S7). In general, our results are in a good agreement with the measurement results of Biskos et al (2006) and the theoretical prediction by Cheng et al. (2015). First, there is a strong size dependence in the hygroscopic growth factor of ammonium sulfate nanoparticles, and smaller ammonium sulfate nanoparticles exhibit lower growth factor at a certain RH. For example, the difference of the growth factor between 6 and 100 nm nanoparticles is up to 0.28 at 80% RH (Fig. S8a). Second, there is, however, no significant size dependence in both DRH and ERH (Fig. S8b). For nanoparticles of different sizes (6-100 nm), the DRH and ERH of ammonium sulfate varies slightly from ~80-83% and ~30-34%, respectively. This variation of the DRH and ERH along the size is much smaller for ammonium sulfate nanoparticles than for sodium chloride (Biskos et al. 2006a, 2007).

Although our results in general agree well with Biskos et al. (2006b), the growth factors of 10, 8, and 6 nm ammonium sulfate nanoparticles that we measured at high RH (i.e., > ~70%) are slightly lower (~0.02 in growth factor) than that in Biskos et al. (2006b) in both deliquescence and efflorescence processes (Fig. 8b and Fig. S7). We calculated the uncertainties of growth factor of 10-nm ammonium sulfate from 80% to 90% RH for our system and Biskos et al. (2006b) system by $\sqrt{\left(\left(g_f \frac{\sqrt{2}\varepsilon_{Dp}}{D_p}\right)^2 + \left(\varepsilon_{RH} \frac{dg_f}{dRH}\right)^2,\right)}$ (Mochida and Kawamura, (2004)). Here, ε_{Dp}, ε_{RH}, and g_f are uncertainty of particle mobility diameter, uncertainty of relative humidity, and growth factor with respect to RH, respectively. The sizing offsets of our system and Biskos et al. (2006b) for 10 nm ammonium sulfate are taken here as $\frac{\varepsilon_{Dp}}{D_p}$ (see Table 1). As shown in the insert of Fig. 8b, the discrepancies between the two systems are still within measurement uncertainty.

In addition, compared to Biskos et al. (2006b), our results show a similar re-structuring in deliquescence mode at RH between about 20% to 75% for 100, and 60 nm ammonium sulfate nanoparticles (Fig 8c). However, different than in Biskos et al. (2006b), we do not find re-structuring for smaller ammonium sulfate nanoparticles (20, 10, 8, and 6 nm) at RH below deliquescence point (Fig. 8c and Fig. 8d). There seems to be continues water adsorption and the adsorbed water layers (Romakkaniemi et al., 2001) become

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

significantly thicker when RH closer to the DRH (i.e, RH > 70%). Note that, the ammonium sulfate hygroscopic data from Biskos et al. (2006b) shown here are all generated by an electrospray, but in our experiments, only the ammonium sulfate nanoparticles with diameters smaller than 20 nm (i.e., 10, 8, and 6 nm) were generated by an electrospray, while the larger nanoparticles (i.e., 20, 60, and 100 nm) were generated by a atomizer. This means the different generation method and drying conditions may influence the surface structure of the nanoparticles and thus their interaction with the adsorbed water layers (Iskandar et al., 2003; Xin et al., 2019).

3.2 Size-dependent hygroscopicity of sodium sulfate nanoparticles

As a common constituent of atmospheric aerosol particles (Tang and Munkelwitz, 1993, 1994; Tang 1996; Tang et al., 2007), hygroscopicity of sodium sulfate with diameters above 20 nm particles has been investigated by a few groups (Tang et al., 2007; Xu and Schweiger, 1999; Hu et al., 2010). However, its hygroscopic behavior in the sub-10 nm size range has not been investigated yet. In this study, we applied our nano-HTDMA system to measure the hygroscopic growth factors, DRH, and ERH of sodium sulfate nanoparticles with dry size from 20 nm down to 6 nm.

Figure 9 shows the measured size-resolved hygroscopic growth factors of sodium sulfate nanoparticles. Different from the observations by Tang et al. (2007) using an electrodynamic balance (EDB), we observed prompt deliquescence and efflorescence for both 20-nm and 6-nm sodium sulfate nanoparticles. Two intersecting modes in the measured number size distribution of humidified sodium sulfate nanoparticles is observed at RH close to the DRH (Fig. S9 and S10 in the Supplementary Information) and ERH, suggesting an externally mixed of aqueous and solid nanoparticles. As shown in Sect. 3.1.3, a similar phenomenon is also observed for ammonium sulfate, which could be attributed to the slight RH heterogeneities in nano-DMA2, which makes only part of the nanoparticles deliquesce at RH close to the DRH, while the others remain in solid state.

Together with the hygroscopic growth of 14-16 µm and 200-20 nm sodium sulfate measured previously by Tang et al. (2007) and Hu et al. (2010), we show a strong size dependence in hygroscopic growth factors of sodium sulfate nanoparticles (Fig. S11d). For example, at RH 84%, the hygroscopic growth factor of 6 nm sodium sulfate is only ~ 1.3 (in efflorescence mode), while the respective growth factors are about 1.5 and 1.8 for 20 nm and 14-16 µm particles. As shown in Fig. 9, E-AIM already agrees well with the hygroscopic growth of micrometer particles (14-16 µm) without shape correction (DeCarlo et al., 2004), i.e., shape factor (χ) of 1.0. However, to explain observation, a shape factor of ~1.16 and 1.26 would be needed for 20 nm and 6 nm sodium sulfate nanoparticles, respectively.

There is no significant change in DRH between 14-16 µm (~84%) and 20 nm (~84%) sodium sulfate particles (Fig. 9). This is consistent with Hu et al. (2010) where no change in DRH from 200 nm down to 20 nm (~82%, see Table 1 from Hu et al. (2010)) was observed. However, a significant increase of DRH occurred when further decreasing particle diameters to 6 nm (DRH = ~90%). The size dependence of ERH is stronger than that of DRH, as there is already a clear increase of ERH from micrometer 14-16 µm (~57%) to 20 nm (~62%) sodium sulfate particles. When further reducing the particle diameters to 6 nm, an almost 6% increase of DRH can be found, compared to the micrometer 14-16 µm particles (i.e., ERH increases from 57 to 82%, respectively). The strong size-effect on the DRH and ERH of sodium chloride and on hygroscopic growth factors of ammonium sulfate have been observed by Biskos et al. (2006a, b, 2007) and theoretically studied and explained by Cheng et al. (2015). Owning to the strong non-ideality of aqueous ammonium sulfate solution, the phase transition concentration (deliquescence and crystallization concentration) of ammonium sulfate is much more sensitivity to the size changes from 60 nm to 6 nm than that of sodium chloride, leading to the almost unchanged DRH and ERH of ammonium sulfate nanoparticles (Cheng et al., 2015). Compared the three compounds, the size-dependent hygroscopicity of sodium sulfate nanoparticles from 20 nm to 6 nm is similar to that of sodium chloride, but different to that of ammonium sulfate, where no significant change in DRH and ERH was observed. However, in this size range, the increase of the ERH and the decrease of growth factor upon decreasing size seems to be stronger for sodium sulfate than sodium chloride, although no significant change in DRH was observed from micrometer size particles down to 20 nm. As different hydrates of sodium sulfate may exist during the deliquescence and efflorescence processes (Xu and Schweiger, 1999), to explain the underline mechanism of the size dependent hygroscopicity of sodium sulfate particles can be challenging.

4 Summary and Conclusion

In this study, we presented our newly designed and self-assembled nano-HTDMA for measuring hygroscopicity of nanoparticles in the sub-10 nm diameter size range. We also introduced the comprehensive methods for system calibration and reported the performance of the system, focusing on the sizing accuracy and preventing pre-deliquescence in the deliquescence measurement mode. By comparing with previous studies on ammonium sulfate nanoparticles (Biskos et al., 2006b), we show that our system is capable of providing high quality data of the hygroscopic behavior of sub-10 nm nanoparticles. We then extended our measurements for sodium sulfate nanoparticles, of which size-dependent deliquescence and efflorescence have been clearly observed for nanoparticles down to 6 nm in size, with similar behavior as sodium chloride.

As we know, atmospheric aerosol particles consist of not only inorganic components, but also a vast number of organic components existing in the atmosphere. However, their physico-chemical properties are still not fully understood, especially when comes to the nano-scale and supersaturated concentration range. The nano-HTDMA system can be directly applicable to explore the size dependence of aerosol nanoparticles. Combing the multi-size measurements of hygroscopicity and the Differential Köhler Analyses (DKA, Cheng et al., 2015) in nano size range, we will be able characterize and parameterize the water activity and surface tension of different inorganic and organic systems. This will further help us to understand the formation and transformation of aerosol nanoparticles in the atmosphere and their interaction with water vapor.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Atmospheric Measurement Techniques Discussions

Data availability

Readers who are interested in the data should contact Yafang Cheng (yafang.cheng@mpic.de).

Acknowledgement

This study was supported by the Max Planck Society (MPG) and Leibniz Society. T.L. acknowledges the support from China Scholarship Council (CSC). Y.C. would like to acknowledge the Minerva Program of MPG.

Author contributions: Y.C. and H.S. designed and led the study. N.M., T.T. and A. W. assembled the basic HTDMA system. Y.C., H.S. and T.L. modified and advanced the basic system into the nano-HTDMA for the purpose of measuring hygroscopic properties of aerosol nanoparticles in sub-10 nm size range at MPIC. T.L. performed the experiments. J.H., N.M. and X.W. supported the experiments. All co-authors discussed the results and commented on the manuscript. T.L. wrote the manuscript with input from all co-authors.

Reference

Andreae, M. O., Afchine, A., Albrecht, R., Holanda, B. A., Artaxo, P., Barbosa, H. M. J., Borrmann, S., Cecchini, M. A., Costa, A., Dollner, M., Fütterer, D., Järvinen, E., Jurkat, T., Klimach, T., Konemann, T., Knote, C., Krämer, M., Krisna, T., Machado, L. A. T., Mertes, S., Minikin, A., Pöhlker, C., Pöhlker, M. L., Pöschl, U., Rosenfeld, D., Sauer, D., Schlager, H., Schnaiter, M., Schneider, J., Schulz, C., Spanu, A., Sperling, V. B., Voigt, C., Walser, A., Wang, J., Weinzierl, B., Wendisch, M., and Ziereis, H.: Aerosol characteristics and particle production in the upper troposphere over the Amazon Basin, Atmos. Chem. Phys., 18, 921-961, 2018.

Badger, C. L., George, I., Griffiths, P. T., Braban, C. F., Cox, R. A., and Abbatt, J. P. D.: Phase transitions and hygroscopic growth of aerosol particles containing humic acid and mixtures of humic acid and ammonium sulphate, Atmospheric Chemistry and Physics, 6, 755-768, 2006.

Bezantakos, S., Huang, L., Barmpounis, K., Martin, S. T., and Biskos, G.: Relative humidity non-uniformities in Hygroscopic Tandem Differential Mobility Analyzer measurements, Journal of Aerosol Science, 101, 1-9, 2016.

Birmili, W., Stratmann, F., Wiedensohler, A., Covert, D., M. Russell, L., and Berg, O.: Determination of Differential Mobility Analyzer Transfer Functions Using Identical Instruments in Series, 1997.

Birmili, W., Weinhold, K., Rasch, F., Sonntag, A., Sun, J., Merkel, M., Wiedensohler, A., Bastian, S., Schladitz, A., Löschau, G., Cyrys, J., Pitz, M., Gu, J., Kusch, T., Flentje, H., Quass, U., Kaminski, H., Kuhlbusch, T. A. J., Meinhardt, F., and Fiebig, M.: Long-term observations of tropospheric particle number size distributions and equivalent black carbon mass concentrations in the German Ultrafine Aerosol Network (GUAN), 2016.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Biskos, G., Malinowski, A., Russell, L. M., Buseck, P. R., and Martin, S. T.: Nanosize Effect on the Deliquescence and the Efflorescence of Sodium Chloride Particles, Aerosol Science and Technology, 40, 97-106, 2006a.

Biskos, G., Paulsen, D., Russell, L. M., Buseck, P. R., and Martin, S. T.: Prompt deliquescence and efflorescence of aerosol nanoparticles, Atmospheric Chemistry and Physics, 6, 4633-4642, 2006b.

Biskos, G., Russell, L. M., Buseck, P. R., and Martin, S. T.: Nanosize effect on the hygroscopic growth factor of aerosol particles, Geophysical Research Letters, 33, 2007.

Chan, M. N. and Chan, C. K.: Hygroscopic properties of two model humic-like substances and their mixtures with inorganics of atmospheric importance, Environmental Science & Technology, 37, 5109-5115, 2003.

Chan, M. N. and Chan. C. K.: Mass transfer effects in hygroscopic measurements of aerosol particles, Atmospheric Chemistry and Physics, 2005.

Chan, M. N., Kreidenweis, S. M., and Chan, C. K.: Measurements of the Hygroscopic and Deliquescence Properties of Organic Compounds of Different Solubilities in Water and Their Relationship with Cloud Condensation Nuclei Activities, Environmental Science & Technology, 42, 3602-3608, 2008.

Chen, Da-Ren, David Y.H. Pui, and Stanley L. Kaufman.: Electrosparing of conducting liquids for monodisperse aerosol generation in the 4 nm to 1.8 µm diameter range, J. Aersosol Sci., 26: 963-977,1995.

Cheng, Y., Su, H., Koop, T., Mikhailov, E., and Poschl, U.: Size dependence of phase transitions in aerosol nanoparticles, Nature communications, 6, 5923, 2015.

Cheng, Y. F., Berghof, M., Garland, R. M., Wiedensohler, A., Wehner, B., Muller, T., Su, H., Zhang, Y. H., Achtert, P., Nowak, A., Poschl, U., Zhu, T., Hu, M., and Zeng, L. M.: Influence of soot mixing state on aerosol light absorption and single scattering albedo during air mass aging at a polluted regional site in northeastern China, Journal of Geophysical Research-Atmospheres, 114, 2009.

Cheng, Y. F., Wiedensohler, A., Eichler, H., Heintzenberg, J., Tesche, M., Ansmann, A., Wendisch, M., Su, H., Althausen, D., Herrmann, H., Gnauk, T., Brüggemann, E., Hu, M., and Zhang, Y. H.: Relative humidity dependence of aerosol optical properties and direct radiative forcing in the surface boundary layer at Xinken in Pearl River Delta of China: An observation based numerical study, Atmospheric Environment, 42, 6373-6397, 2008.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: Thermodynamic Model of the System $H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O$ at Tropospheric Temperatures, The Journal of Physical Chemistry A, 102, 2137-2154, 1998.

Collins, D. R., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: The Scanning DMA Transfer Function, Aerosol Science and Technology, 38, 833-850, 2004.

Cruz, C. N. and Pandis, S. N.: Deliquescence and Hygroscopic Growth of Mixed Inorganic−Organic Atmospheric Aerosol, Environmental Science & Technology, 34, 4313-4319, 2000.

DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 1: Theory, Aerosol Science and Technology, 38, 1185-1205, 2004.

Dong, J. L., Xiao, H. S., Zhao, L. J., and Zhang, Y.-H.: Spatially resolved Raman investigation on phase separations of mixed $Na_2SO_4/MgSO_4$ droplets, 2009.

Dougle, P. G., Veefkind, J. P., and ten Brink, H. M.: Crystallisation of mixtures of ammonium nitrate, ammonium sulphate and soot, Journal of Aerosol Science, 29, 375-386, 1998.

Dunne, E. M., Gordon, H., Kürten, A., Almeida, J., Duplissy, J., Williamson, C., Ortega, I. K., Pringle, K. J., Adamov, A., Baltensperger, U., Barmet, P., Benduhn, F., Bianchi, F., Breitenlechner, M., Clarke, A., Curtius, J., Dommen, J., Donahue, N. M., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Jokinen, T., Kangasluoma, J., Kirkby, J., Kulmala, M., Kupc, A., Lawler, M. J., Lehtipalo, K., Makhmutov, V., Mann, G., Mathot, S., Merikanto, J., Miettinen, P., Nenes, A., Onnela, A., Rap, A., Reddington, C. L. S., Riccobono, F., Richards, N. A. D., Rissanen, M. P., Rondo, L., Sarnela, N., Schobesberger, S., Sengupta, K., Simon, M., Sipilä, M., Smith, J. N., Stozkhov, Y., Tomé, A., Tröstl, J., Wagner, P. E., Wimmer, D., Winkler, P. M., Worsnop, D. R., and Carslaw, K. S.: Global atmospheric particle formation from CERN CLOUD measurements, Science, 354, 1119-1124, 2016.

Duplissy, J., Gysel, M., S, S., Meyer, N., N, G., L, K., V, M., R, W., Martins dos Santos, S., C, G., Villani, P., P, L., Sellegri, K., A, M., B. McFiggans, G., G, W., R, R., Dommen, J., Ristovski, Z., and Weingartner, E.: Intercomparison study of six HTDMAs: results and general recommendations for HTDMA operation, Atmospheric Measurement Techniques, 2. Pp, 363-378, 2009.

Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, Nature, 506, 476, 2014.

Eichler, H., Cheng, Y., Birmili, W., Nowak, A., Wiedensohler, A., Brüggemann, E., Gnauk, T., Herrmann, H., Althausen, D., Ansmann, A., Engelmann, R., Tesche, M., Wendisch, M., Zhang, Y. H., Hu, M., Liu, S., and Zeng, L.: Hygroscopic properties and extinction of aerosol particles at ambient relative humidity in South-Eastern China, 2008.

Estillore, A. D., Morris, H. S., Or, V. W., Lee, H. D., Alves, M. R., Marciano, M. A., Laskina, O., Qin, Z., Tivanski, A. V., and Grassian, V. H.: Linking hygroscopicity and the surface microstructure of model

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

inorganic salts, simple and complex carbohydrates, and authentic sea spray aerosol particles, Physical Chemistry Chemical Physics, 19, 21101-21111, 2017.

Fan, J., Rosenfeld, D., Zhang, Y., Giangrande, S. E., Li, Z., Machado, L. A. T., Martin, S. T., Yang, Y., Wang, J., Artaxo, P., Barbosa, H. M. J., Braga, R. C., Comstock, J. M., Feng, Z., Gao, W., Gomes, H. B., Mei, F., Pöhlker, C., Pöhlker, M. L., Pöschl, U., and de Souza, R. A. F.: Substantial convection and precipitation enhancements by ultrafine aerosol particles, Science, 359, 411-418, 2018.

Gao, Y., Chen, S. B., and Yu, L. E.: Efflorescence Relative Humidity for Ammonium Sulfate Particles, The Journal of Physical Chemistry A, 110, 7602-7608, 2006.

Ghorai, S., Wang, B., Tivanski, A., and Laskin, A.: Hygroscopic Properties of Internally Mixed Particles Composed of NaCl and Water-Soluble Organic Acids, Environmental Science & Technology, 48, 2234-2241, 2014.

Giamarelou, M., Smith, M., Papapanagiotou, E., Martin, S. T., and Biskos, G.: Hygroscopic properties of potassium-halide nanoparticles, Aerosol Science and Technology, 52, 536-545, 2018.

Gysel, M., Weingartner, E., and Baltensperger, U.: Hygroscopicity of aerosol particles at low temperatures. 2. Theoretical and experimental hygroscopic properties of laboratory generated aerosols, Environmental Science & Technology, 36, 63-68, 2002.

Hämeri, K., Laaksonen, A., Väkevä, M., and Suni, T.: Hygroscopic growth of ultrafine sodium chloride particles, Journal of Geophysical Research: Atmospheres, 106, 20749-20757, 2001.

Hämeri, K., Väkevä, M., Hansson, H.-C., and Laaksonen, A.: Hygroscopic growth of ultrafine ammonium sulfate aerosol measured using an ultrafine tandem differential mobility analyzer, Journal of Geophysical Research: Atmospheres, 105, 22231-22242, 2000.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Hansson, H.-C., Rood, M. J., Koloutsou-Vakakis, S., Hämeri, K., Orsini, D., and Wiedensohler, A.: NaCl Aerosol Particle Hygroscopicity Dependence on Mixing with Organic Compounds, Journal of Atmospheric Chemistry, 31, 321-346, 1998.

Hennig, T., Massling, A., Brechtel, F. J., and Wiedensohler, A.: A tandem DMA for highly temperature-stabilized hygroscopic particle growth measurements between 90 % and 98% relative humidity, Journal of Aerosol Science, 36, 1210-1223, 2005.

Hong, J., Häkkinen, S. A. K., Paramonov, M., Äijälä, M., Hakala, J., Nieminen, T., Mikkilä, J., Prisle, N. L., Kulmala, M., Riipinen, I., Bilde, M., Kerminen, V. M., and Petäjä, T.: Hygroscopicity, CCN and volatility properties of submicron atmospheric aerosol in a boreal forest environment during the summer of 2010, Atmos. Chem. Phys., 14, 4733-4748, 2014.

Hong, J., Kim, J., Nieminen, T., Duplissy, J., Ehn, M., Äijälä, M., Hao, L. Q., Nie, W., Sarnela, N., Prisle, N. L., Kulmala, M., Virtanen, A., Petäjä, T., and Kerminen, V. M.: Relating the hygroscopic properties of submicron aerosol to both gas- and particle-phase chemical composition in a boreal forest environment, Atmos. Chem. Phys., 15, 11999-12009, 2015.

Hu, D., Qiao, L., Chen, J.-M., Ye, X., Yang, X., Cheng, T., and Fang, W.: Hygroscopicity of Inorganic Aerosols: Size and Relative Humidity Effects on the Growth Factor, 2010.

Iskandar, F., Gradon, L., and Okuyama, K.: Control of the morphology of nanostructured particles prepared by the spray drying of a nanoparticle sol, Journal of Colloid and Interface Science, 265, 296-303, 2003.

Kerminen, V. M.: The effects of particle chemical character and atmospheric processes on particle hygroscopic properties, Journal of Aerosol Science, 28, 121-132, 1997.

Keskinen, H., Virtanen, A., Joutsensaari, J., Tsagkogeorgas, G., Duplissy, J., Schobesberger, S., Gysel, M., Riccobono, F., Slowik, J. G., Bianchi, F., Yli-Juuti, T., Lehtipalo, K., Rondo, L., Breitenlechner, M., Kupc, A., Almeida, J., Amorim, A., Dunne, E. M., Downard, A. J., Ehrhart, S., Franchin, A., Kajos, M. K., Kirkby, J., Kürten, A., Nieminen, T., Makhmutov, V., Mathot, S., Miettinen, P., Onnela, A., Petäjä, T., Praplan, A., Santos, F. D., Schallhart, S., Sipilä, M., Stozhkov, Y., Tomé, A., Vaattovaara, P., Wimmer, D., Prevot, A., Dommen, J., Donahue, N. M., Flagan, R. C., Weingartner, E., Viisanen, Y., Riipinen, I., Hansel, A., Curtius, J., Kulmala, M., Worsnop, D. R., Baltensperger, U., Wex, H., Stratmann, F., and Laaksonen, A.: Evolution of particle composition in CLOUD nucleation experiments, Atmos. Chem. Phys., 13, 5587-5600, 2013.

Kim, J., Ahlm, L., Yli-Juuti, T., Lawler, M., Keskinen, H., Tröstl, J., Schobesberger, S., Duplissy, J., Amorim, A., Bianchi, F., Donahue, N. M., Flagan, R. C., Hakala, J., Heinritzi, M., Jokinen, T., Kürten, A., Laaksonen, A., Lehtipalo, K., Miettinen, P., Petäjä, T., Rissanen, M. P., Rondo, L., Sengupta, K., Simon, M., Tomé, A., Williamson, C., Wimmer, D., Winkler, P. M., Ehrhart, S., Ye, P., Kirkby, J., Curtius, J., Baltensperger, U., Kulmala, M., Lehtinen, K. E. J., Smith, J. N., Riipinen, I., and Virtanen, A.: Hygroscopicity of nanoparticles produced from homogeneous nucleation in the CLOUD experiments, Atmos. Chem. Phys., 16, 293-304, 2016.

Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R. C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E. R., Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petäjä, T., Schnitzhofer, R., Seinfeld, J. H., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P. E., Walther, H., Weingartner, E., Wex, H., Winkler, P. M., Carslaw, K. S., Worsnop, D. R., Baltensperger, U., and Kulmala, M.: Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476, 429-433, 2011.

Köhler, H.: The nucleus in and the growth of hygroscopic droplets, Transactions of the Faraday Society, 32, 1152-1161, 1936.

Kreidenweis, S. M., Koehler, K., DeMott, P. J., Prenni, A. J., Carrico, C., and Ervens, B.: Water activity and activation diameters from hygroscopicity data - Part I: Theory and application to inorganic salts, Atmospheric Chemistry and Physics, 5, 1357-1370, 2005.

Lei, T., Zuend, A., Cheng, Y., Su, H., Wang, W., and Ge, M.: Hygroscopicity of organic surrogate compounds from biomass burning and their effect on the efflorescence of ammonium sulfate in mixed aerosol particles, Atmos. Chem. Phys., 18, 1045-1064, 2018.

Lei, T., Zuend, A., Wang, W. G., Zhang, Y. H., and Ge, M. F.: Hygroscopicity of organic compounds from biomass burning and their influence on the water uptake of mixed organic ammonium sulfate aerosols, Atmos. Chem. Phys., 14, 11165-11183, 2014.

Lihavainen, H., Kerminen, V.-M., Komppula, M., Hatakka, J., Aaltonen, V., Kulmala, M., and Viisanen, Y.: Production of "potential" cloud condensation nuclei associated with atmospheric new-particle formation in northern Finland, Journal of Geophysical Research: Atmospheres, 108, 2003.

Martin, S. T.: Phase Transitions of Aqueous Atmospheric Particles, Chemical Reviews, 100, 3403-3454, 2000.

Massling, A., Niedermeier, N., Hennig, T., Fors, E. O., Swietlicki, E., Ehn, M., Hämeri, K., Villani, P., Laj, P., Good, N., McFiggans, G., and Wiedensohler, A.: Results and recommendations from an intercomparison of six Hygroscopicity-TDMA systems, Atmos. Meas. Tech., 4, 485-497, 2011.

McMurry, P. H.: A review of atmospheric aerosol measurements, Atmospheric Environment, 34, 1959-1999, 2000.

Mikhailov, E., Vlasenko, S., Martin, S. T., Koop, T., and Poschl, U.: Amorphous and crystalline aerosol particles interacting with water vapor: conceptual framework and experimental evidence for restructuring, phase transitions and kinetic limitations, Atmospheric Chemistry and Physics, 9, 9491-9522, 2009.

Mikhailov, E., Vlasenko, S., Niessner, R., and Poschl, U.: Interaction of aerosol particles composed of protein and salts with water vapor: hygroscopic growth and microstructural rearrangement, Atmospheric Chemistry and Physics, 4, 323-350, 2004.

Mikhailov, E., Vlasenko, S., Rose, D., and Pöschl, U.: Mass-based hygroscopicity parameter interaction model and measurement of atmospheric aerosol water uptake, Atmos. Chem. Phys., 13, 717-740, 2013.

Mikhailov, E. F. and Vlasenko, S. S.: High humidity tandem differential mobility analyzer for accurate determination of aerosol hygroscopic growth, microstructure and activity coefficients over a wide range of relative humidity, Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2019-478, in review, 2019.

Mikhailov, E. F., Vlasenko, S. S., and Ryshkevich, T. I.: Influence of chemical composition and microstructure on the hygroscopic growth of pyrogenic aerosol, Izvestiya, Atmospheric and Oceanic Physics, 44, 416-431, 2008.

Mirabel, P., Reiss, H., and Bowles, R. K.: A theory for the deliquescence of small particles, The Journal of Chemical Physics, 113, 8200-8205, 2000.

Mochida, M. and Kawamura, K.: Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles, Journal of Geophysical Research-Atmospheres, 109, 2004.

Mulholland, G. W., Donnelly, M. K., Hagwood, C. R., Kukuck, S. R., Hackley, V. A., and Pui, D. Y. H.: Measurement of 100 nm and 60 nm Particle Standards by Differential Mobility Analysis, Journal of Research of the National Institute of Standards and Technology, 111, 257-312, 2006.

Park, K., Kim, J.-S., and Miller, A. L.: A study on effects of size and structure on hygroscopicity of nanoparticles using a tandem differential mobility analyzer and TEM, Journal of Nanoparticle Research, 11, 175-183, 2009.

Peng, C., Chow, A. H. L., and Chan, C. K.: Hygroscopic Study of Glucose, Citric Acid, and Sorbitol Using an Electrodynamic Balance: Comparison with UNIFAC Predictions, Aerosol Science and Technology, 35, 753-758, 2001.

Pope, F. D., Dennis-Smither, B. J., Griffiths, P. T., Clegg, S. L., and Cox, R. A.: Studies of Single Aerosol Particles Containing Malonic Acid, Glutaric Acid, and Their Mixtures with Sodium Chloride. I. Hygroscopic Growth, The Journal of Physical Chemistry A, 114, 5335-5341, 2010.

Pruppacher, H. R. & Klett, J. D: Microphysics of clouds and precipitation, Kluwer Academic Publishers, 1997.

Rader, D. J. and McMurry, P. H.: Application of the tandem differential mobility analyzer to studies of droplet growth or evaporation, Journal of Aerosol Science, 17, 771-787, 1986.

Raoux, S., Rettner, C. T., Jordan-Sweet, J. L., Kellock, A. J., Topuria, T., Rice, P. M., and Miller, D. C.: Direct observation of amorphous to crystalline phase transitions in nanoparticle arrays of phase change materials, Journal of Applied Physics, 102, 094305, 2007.

Reid, J. P., Dennis-Smither, B. J., Kwamena, N.-O. A., Miles, R. E. H., Hanford, K. L., and Homer, C. J.: The morphology of aerosol particles consisting of hydrophobic and hydrophilic phases: hydrocarbons, alcohols and fatty acids as the hydrophobic component, Physical Chemistry Chemical Physics, 13, 15559-15572, 2011.

Richardson, C. B. and Spann, J.: Measurement of Water Cycle in a Levitated Ammonium Sulfate Particles, 1984.

Rickards, A. M. J., Miles, R. E. H., Davies, J. F., Marshall, F. H., and Reid, J. P.: Measurements of the Sensitivity of Aerosol Hygroscopicity and the κ Parameter to the O/C Ratio, The Journal of Physical Chemistry A, 117, 14120-14131, 2013.

Romakkaniemi, S., Hämeri, K., Väkevä, M., and Laaksonen, A.: Adsorption of Water on 8−15 nm NaCl and $(NH_4)_2SO_4$ Aerosols Measured Using an Ultrafine Tandem Differential Mobility Analyzer, The Journal of Physical Chemistry A, 105, 8183-8188, 2001.

Russell, L. M. and Ming, Y.: Deliquescence of small particles, Journal of Chemical Physics, 116, 311-321, 2002.

Sakurai, H., A. Fink, M., H. McMurry, P., Mauldin, R., F. Moore, K., N. Smith, J., and Eisele, F.: Hygroscopicity and volatility of 4–10 nm particles during summertime atmospheric nucleation events in urban Atlanta, 2005.

Seinfeld, J. H., and S. N. Pandis: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd ed., John Wiley, New York, 2006.

Sihto, S. L., Mikkilä, J., Vanhanen, J., Ehn, M., Liao, L., Lehtipalo, K., Aalto, P. P., Duplissy, J., Petäjä, T., Kerminen, V. M., Boy, M., and Kulmala, M.: Seasonal variation of CCN concentrations and aerosol activation properties in boreal forest, Atmos. Chem. Phys., 11, 13269-13285, 2011.

Stock, M., Cheng, Y. F., Birmili, W., Massling, A., Wehner, B., Müller, T., Leinert, S., Kalivitis, N., Mihalopoulos, N., and Wiedensohler, A.: Hygroscopic properties of atmospheric aerosol particles over the Eastern Mediterranean: implications for regional direct radiative forcing under clean and polluted conditions, Atmos. Chem. Phys., 11, 4251-4271, 2011.

Su, H., Rose, D., Cheng, Y. F., Gunthe, S. S., Massling, A., Stock, M., Wiedensohler, A., Andreae, M. O., and Pöschl, U.: Hygroscopicity distribution concept for measurement data analysis and modeling of aerosol

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

particle mixing state with regard to hygroscopic growth and CCN activation, Atmos. Chem. Phys., 10, 7489-7503, 2010.

Tang, I. N.: Chemical and size effects of hygroscopic aerosols on light scattering coefficients, Journal of Geophysical Research: Atmospheres, 101, 19245-19250, 1996.

Tang, I. N., Fung, K. H., Imre, D. G., and Munkelwitz, H. R.: Phase Transformation and Metastability of Hygroscopic Microparticles, Aerosol Science and Technology, 23, 443-453, 2007.

Tang, I. N. and Munkelwitz, H. R.: Composition and temperature dependence of the deliquescence properties of hygroscopic aerosols, Atmospheric Environment. Part A. General Topics, 27, 467-473, 1993.

Tang, I. N. and Munkelwitz, H. R.: Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance, Journal of Geophysical Research: Atmospheres, 99, 18801-18808, 1994.

Tang, M., Chan, C. K., Li, Y. J., Su, H., Ma, Q., Wu, Z., Zhang, G., Wang, Z., Ge, M., Hu, M., He, H., and Wang, X.: A review of experimental techniques for aerosol hygroscopicity studies, Atmos. Chem. Phys., 19, 12631-12686, 2019.

Topping, D., McFiggans, G., and Coe, H.: A curved multi-component aerosol hygroscopicity model framework: Part 1–Inorganic compounds, Atmospheric Chemistry and Physics, 5, 1205-1222, 2005.

Villani, P., Picard, D., Michaud, V., Laj, P., and Wiedensohler, A.: 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 Science and Technology, 42, 729-741, 2008.

Vlasenko, S. S., Su, H., Pöschl, U., Andreae, M. O., and Mikhailov, E. F.: Tandem configuration of differential mobility and centrifugal particle mass analysers for investigating aerosol hygroscopic properties, Atmos. Meas. Tech., 10, 1269-1280, 2017.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Wang, J., Krejci, R., Giangrande, S., Kuang, C., Barbosa, H. M. J., Brito, J., Carbone, S., Chi, X., Comstock, J., Ditas, F., Lavric, J., Manninen, H. E., Mei, F., Moran-Zuloaga, D., Pöhlker, C., Pöhlker, M. L., Saturno, J., Schmid, B., Souza, R. A. F., Springston, S. R., Tomlinson, J. M., Toto, T., Walter, D., Wimmer, D., Smith, J. N., Kulmala, M., Machado, L. A. T., Artaxo, P., Andreae, M. O., Petäjä, T., and Martin, S. T.: Amazon boundary layer aerosol concentration sustained by vertical transport during rainfall, Nature, 539, 416, 2016.

Wang, L., Khalizov, A. F., Zheng, J., Xu, W., Ma, Y., Lal, V., and Zhang, R.: Atmospheric nanoparticles formed from heterogeneous reactions of organics, Nature Geoscience, 3, 238, 2010.

Wang, X., Ma, N., Lei, T., Größ, J., Li, G., Liu, F., Meusel, H., Mikhailov, E., Wiedensohler, A., and Su, H.: Effective density and hygroscopicity of protein particles generated with spray-drying process, Journal of Aerosol Science, 137, 105441, 2019.

Wang, Z., Su, H., Wang, X., Ma, N., Wiedensohler, A., Pöschl, U., and Cheng, Y.: Scanning supersaturation condensation particle counter applied as a nano-CCN counter for size-resolved analysis of the hygroscopicity and chemical composition of nanoparticles, Atmos. Meas. Tech., 8, 2161-2172, https://doi.org/10.5194/amt-8-2161-2015, 2015.

Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., Tuch, T., Pfeifer, S., Fiebig, M., Fjäraa, A. M., Asmi, E., Sellegri, K., Depuy, R., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J. A., Swietlicki, E., Williams, P., Roldin, P., Quincey, P., Hüglin, C., Fierz-Schmidhauser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Grüning, C., Faloon, K., Beddows, D., Harrison, R., Monahan, C., Jennings, S. G., O'Dowd, C. D., Marinoni, A., Horn, H. G., Keck, L., Jiang, J., Scheckman, J., McMurry, P. H., Deng, Z., Zhao, C. S., Moerman, M., Henzing, B., de Leeuw, G., Löschau, G., and Bastian, S.: Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions, Atmos. Meas. Tech., 5, 657-685, 2012.

Wiedensohler, A., Cheng, Y. F., Nowak, A., Wehner, B., Achtert, P., Berghof, M., Birmili, W., Wu, Z. J., Hu, M., Zhu, T., Takegawa, N., Kita, K., Kondo, Y., Lou, S. R., Hofzumahaus, A., Holland, F., Wahner, A., Gunthe, S. S., Rose, D., Su, H., and Pöschl, U.: Rapid aerosol particle growth and increase of cloud condensation nucleus activity by secondary aerosol formation and condensation: A case study for regional air pollution in northeastern China, Journal of Geophysical Research: Atmospheres, 114, 2009.

Wiedensohler, A., Wiesner, A., Weinhold, K., Birmili, W., Hermann, M., Merkel, M., Müller, T., Pfeifer, S., Schmidt, A., Tuch, T., Velarde, F., Quincey, P., Seeger, S., and Nowak, A.: Mobility particle size spectrometers: Calibration procedures and measurement uncertainties, Aerosol Science and Technology, 52, 146-164, 2018.

Wise, M. E., Surratt, J. D., Curtis, D. B., Shilling, J. E., and Tolbert, M. A.: Hygroscopic growth of ammonium sulfate/dicarboxylic acids, Journal of Geophysical Research-Atmospheres, 108, 2003.

Wu, Z. J., Nowak, A., Poulain, L., Herrmann, H., and Wiedensohler, A.: Hygroscopic behavior of atmospherically relevant water-soluble carboxylic salts and their influence on the water uptake of ammonium sulfate, Atmos. Chem. Phys., 11, 12617-12626, 2011.

Xu, B. and Schweiger, G.: In-situ Raman observation of phase transformation of Na2SO4 during the hydration/dehydration cycles on single levitated microparticle, 1999.

You, Y., Renbaum-Wolff, L., and Bertram, A. K.: Liquid–liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride, Atmos. Chem. Phys., 13, 11723-11734, 2013.

Zawadowicz, M. A., Proud, S. R., Seppalainen, S. S., and Cziczo, D. J.: Hygroscopic and phase separation properties of ammonium sulfate/organics/water ternary solutions, Atmos. Chem. Phys., 15, 8975-8986, 2015.

Zhang, S. L., Ma, N., Kecorius, S., Wang, P. C., Hu, M., Wang, Z. B., Größ, J., Wu, Z. J., and Wiedensohler, A.: Mixing state of atmospheric particles over the North China Plain, Atmospheric Environment, 125, 152-164, 2016.

Zhao, L.-J., Zhang, Y.-H., Wei, Z.-F., Cheng, H., and Li, X.-H.: Magnesium Sulfate Aerosols Studied by FTIR Spectroscopy: Hygroscopic Properties, Supersaturated Structures, and Implications for Seawater Aerosols, The Journal of Physical Chemistry A, 110, 951-958, 2006.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Atmospheric Measurement Techniques Discussions

Tables

Table 1. Accuracy, precision and sources of uncertainty associated with HTDMA measurements.

	Biskos et al. (2006b)	Hämeri et al. (2000)	Nano-HTDMA (This study)
DMA System			
Type of DMA1 & DMA2	TSI nano-DMAs	Hauke-type DMAs	Vienna-type short DMAs
Accuracy of aerosol flow in DMA2	±1% (0.3-1.5 l/min)	-	±1% (1.5 l/min)
Accuracy of sheath flow in DMA2	±1% (5-15 l/min)	-	±1% (10 l/min)
Accuracy of DMA voltage	±0.1% (0-500V)	-	±0.1% (0-350V)
Sizing accuracy of DMA2 using PSL	3%	-	0.4% (100-nm PSL)
Sizing agreement between DMAs using ammonium sulfate	3.1% (10 nm) [a]	±1% [b]	0.6% (100 nm) [c] 0.5% (60 nm) [c] 1.4% (20 nm) [c] 0.9% (10 nm) [c] -0.2% (8 nm) [c] 1.4% (6 nm) [c]
Precision of particle-sizing	<2%	-	<2% (6-200 nm) [d]

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Humidification System			
Type of RH sensor	RH sensors (Omega Model HX93AV)	Dew point mirror (GE) RH sensors (Vaisala Humitter model 50Y)	Dew point mirror (Edge) RH sensors (Vaisala model HMT 330)
Accuracy of RH sensors (0-90% RH)	±2.5% RH	±3% RH [e]	±1% (RH sensor)
Position of the probe in the system	Inlet of DMA2 (RH_a sensor [f], RH_s sensor [g])	Inlet of DMA2 (RH_a sensor) & excess air (RH_s sensor, dew point mirror)	Inlet of DMA2 (RH_a sensor, RH_s sensor) & excess air (dew point mirror)
RH setting	$RH_a=RH_s$	$RH_s \geqslant RH_a+3\%$	$RH_a=RH_s$
Temperature Control System			
Temperature control type	Thermally isolated environment (humidification+DMA2)[h]	Thermally isolated environment (DMA2)	Box T regulated (humidification+DMA2)
Difference in T between inlet and outlet of DMA2	-	-	<0.2°C

[-] Not reported.
[a] According to the scans of the second DMA for the hygroscopic growth of 10 nm ammonium sulfate and the growth factors at different RHs provided by Biskos et al. (2006b), we retrieved an average sizing offset of Biskos et al. (2006b) system to be ~3.1% at 10 nm (see SI, S1).
[b] Size range not given.
[c] See Table S2 in supporting information.
[d] Value calculated according to the relative standard derivation.
[e] From Vaisala Humitter model 50Y manual.
[f] RH_a: the RH of aerosol flow.
[g] RH_s: the RH of sheath flow.
[h] Bezantakos et al. (2016).

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Figures

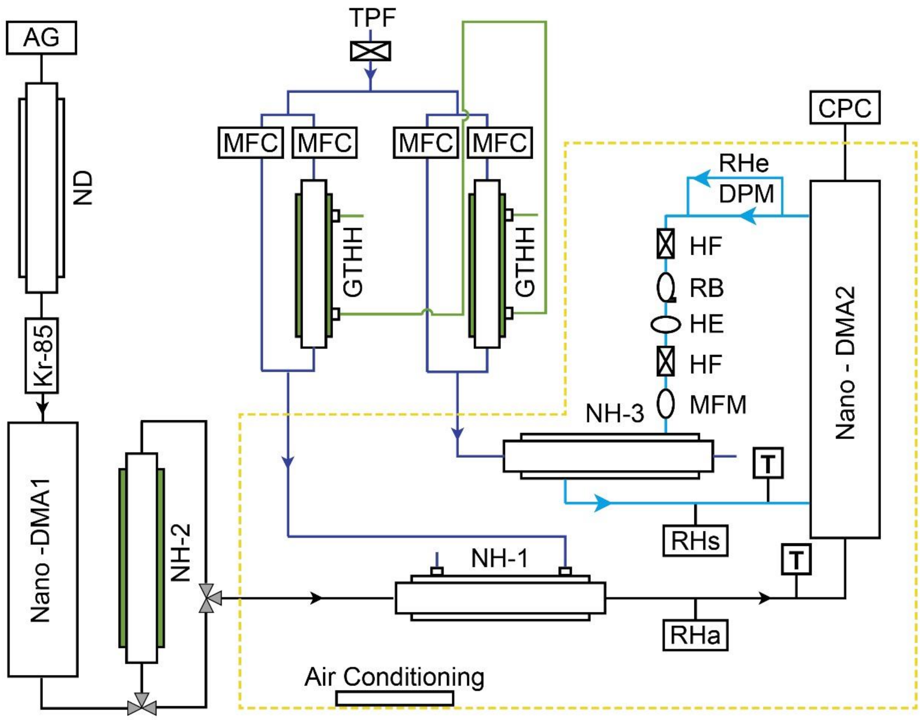


Figure 1. Experimental setup of the nano-HTDMA. Here, AG: aerosol generator (aerosol atomizer or electrospray); ND: nafion dryer; Kr-85: Krypton source aerosol neutralizer; Nano-DMA: nano differential mobility analyzer; TPF: total particle filter; HF: hydrophobic filter; MFC: mass flow controller; MFM: mass flow meter; RB: recirculation blower; DPM: dew point mirror; GTHH: Gore-Tex humidifier and heater; NH: nafion humidifier; HE: heat exchanger; CPC: condensation particle counter; Black line: aerosol line; Blue line: sheath line; Royal blue line: humidified air; Green line: MilliQ water (resistivity of 18.2 MΩ cm at 298.15 K). RH_a and RH_s (measured by RH sensors) represent the RH of aerosol and sheath flow in the inlet of nano-DMA2, respectively. RH_e (measured by dew point) represents the RH of excess air. T represent the temperature of aerosol and sheath flow in the inlet of nano-DMA2, respectively.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Atmospheric Measurement Techniques Discussions

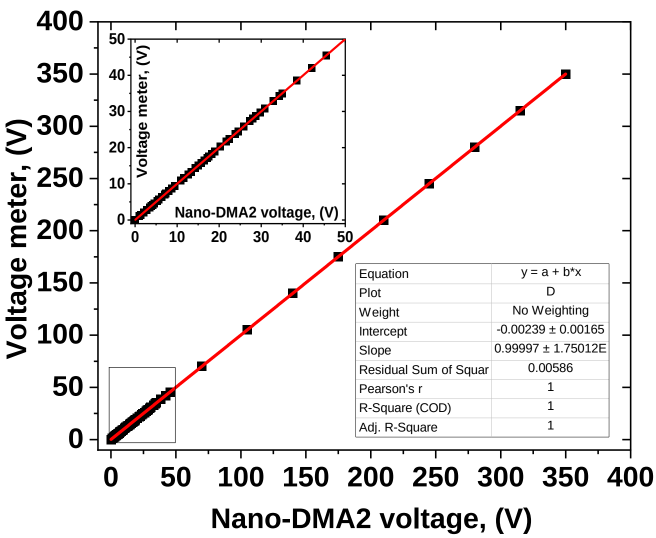


Figure 2. An example of voltage calibration of the nano-DMA2.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

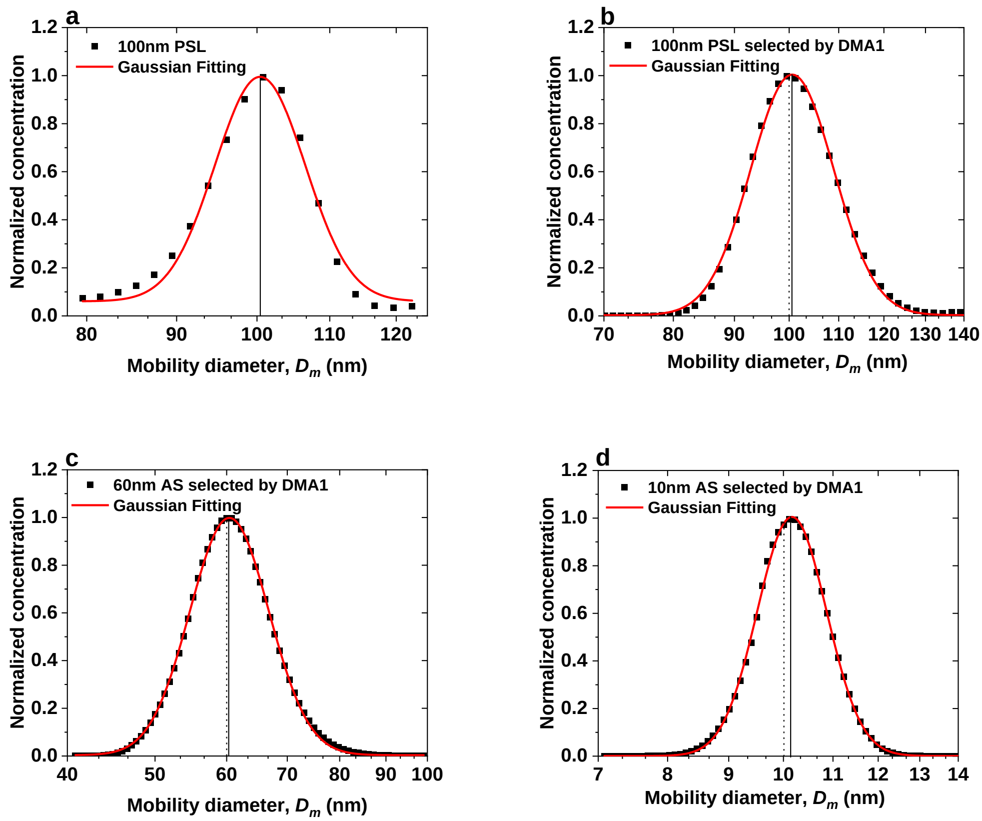


Figure 3. Sizing accuracy and sizing offset of nano-DMAs after calibration. **(a)** Normalized number size distribution scanned by the nano-DMA2 for 100-nm PSL nanoparticles (black solid square). The black solid line marks peak diameter from the Gaussian fits for the scan (red curve). Normalized number size distributions scanned by the nano-DMA2 for 100-nm PSL nanoparticles **(b)**, 60-nm **(c)**, and 10-nm **(d)** ammonium sulfate (AS) selected by the nano-DMA1 at RH below 5% at 298 K (black solid square). The dotted lines mark the diameters of the monodispersed nanoparticles selected by the nano-DMA1, i.e., 100 nm in **(b)**, 60 nm in **(c)** and 10 nm in **(d)**. The black solid lines mark the peak diameters from the Gaussian fits (red curve).

Atmospheric Measurement Techniques
Discussions

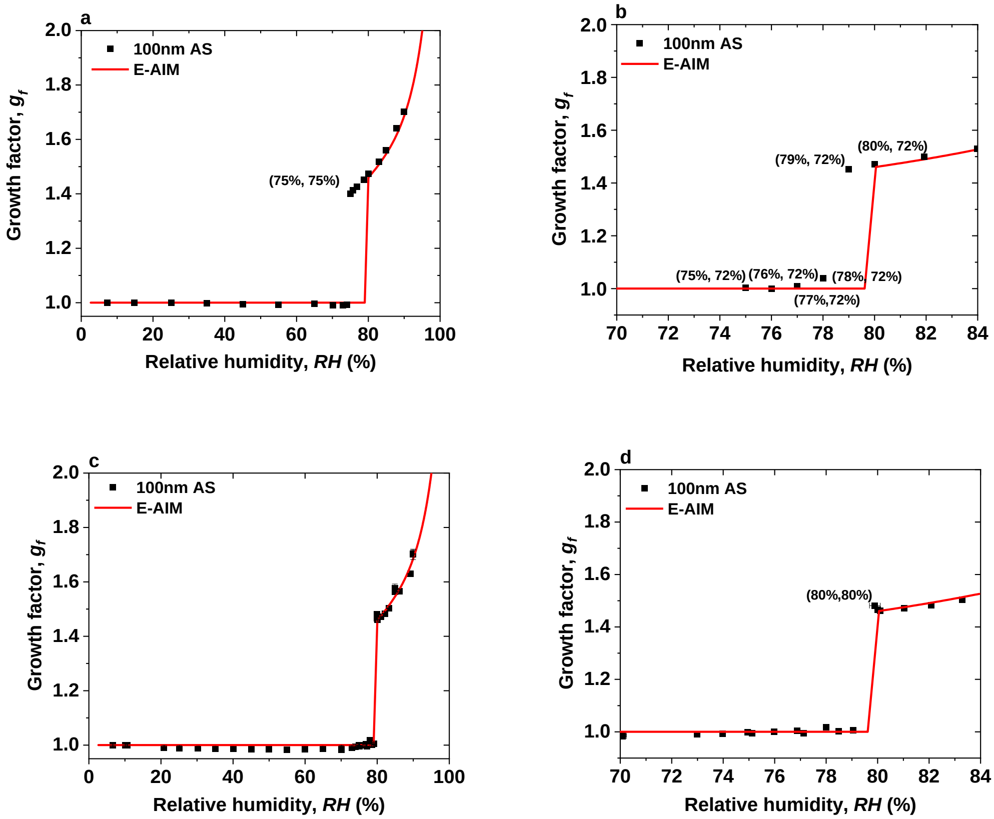
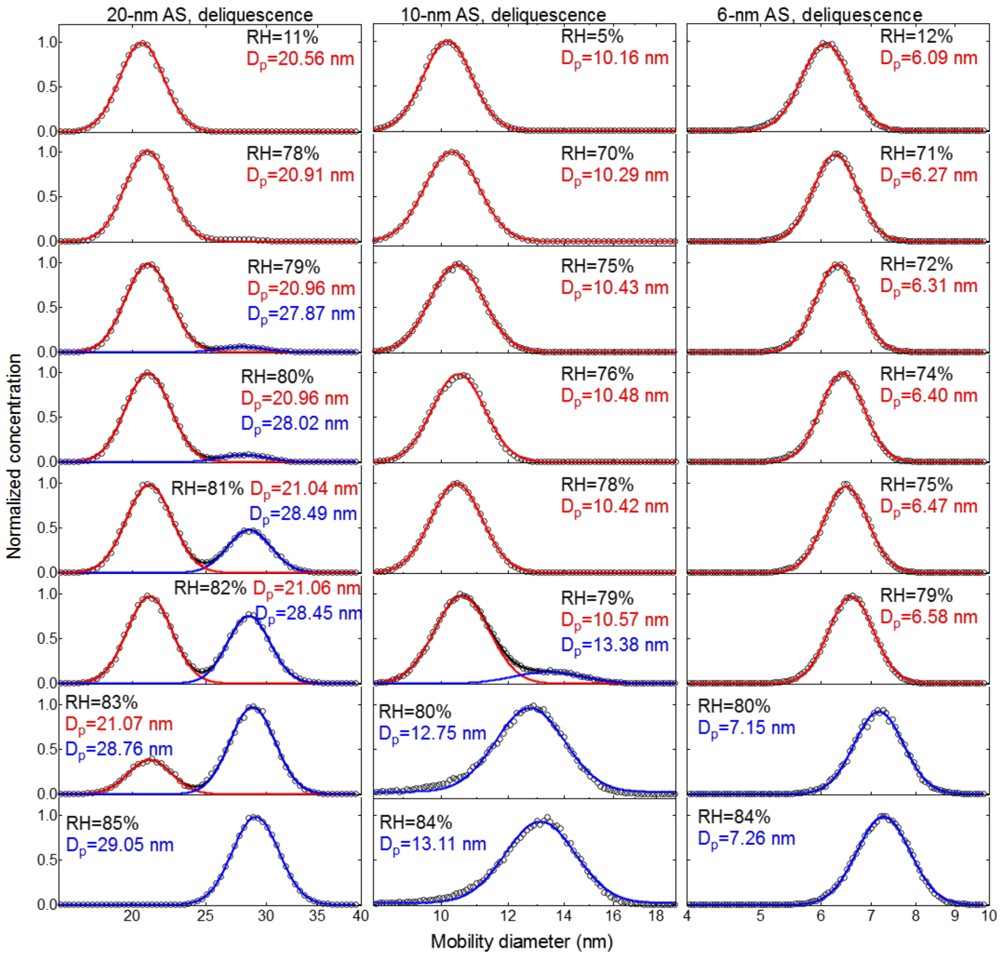


Figure 4. Mobility-diameter hygroscopic growth factors (g_f) of 100-nm ammonium sulfate (AS) nanoparticles at 298 K measured in deliquescence mode. In comparison, the E-AIM model predicted growth factors of ammonium sulfate nanoparticles at 100 nm. **(a) RH_e=RH_a**, (75%, 75%) represents the (RH_e, RH_a), **(b) $RH_e \geq RH_a$+3%**, (75%, 72%) represents the (RH_e, RH_a), and **(c) RH_s = RH_a**. **(d)** The enlarged view of the RH range of 70% to 84% in Fig. 4c. (80%, 80%) represents the (RH_s, RH_a). RH_s and RH_e are the RH of sheath flow in the inlet of nano-DMA2 and in the excess air line, respectively; RH_a is the RH of aerosol flow in the inlet of nano-DMA2.

Atmospheric Measurement Techniques Discussions



906

907 **Figure 5.** Deliquescence-mode measurements of ammonium sulfate (AS) aerosol nanoparticles with dry mobility
908 diameter from 20-6nm. The measured (black square) and fitted (solid lines) normalized size distribution are shown for
909 increasing RH. The RH history in each measurement is 5% → X%, where X is the RH value given in each panel.

910

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

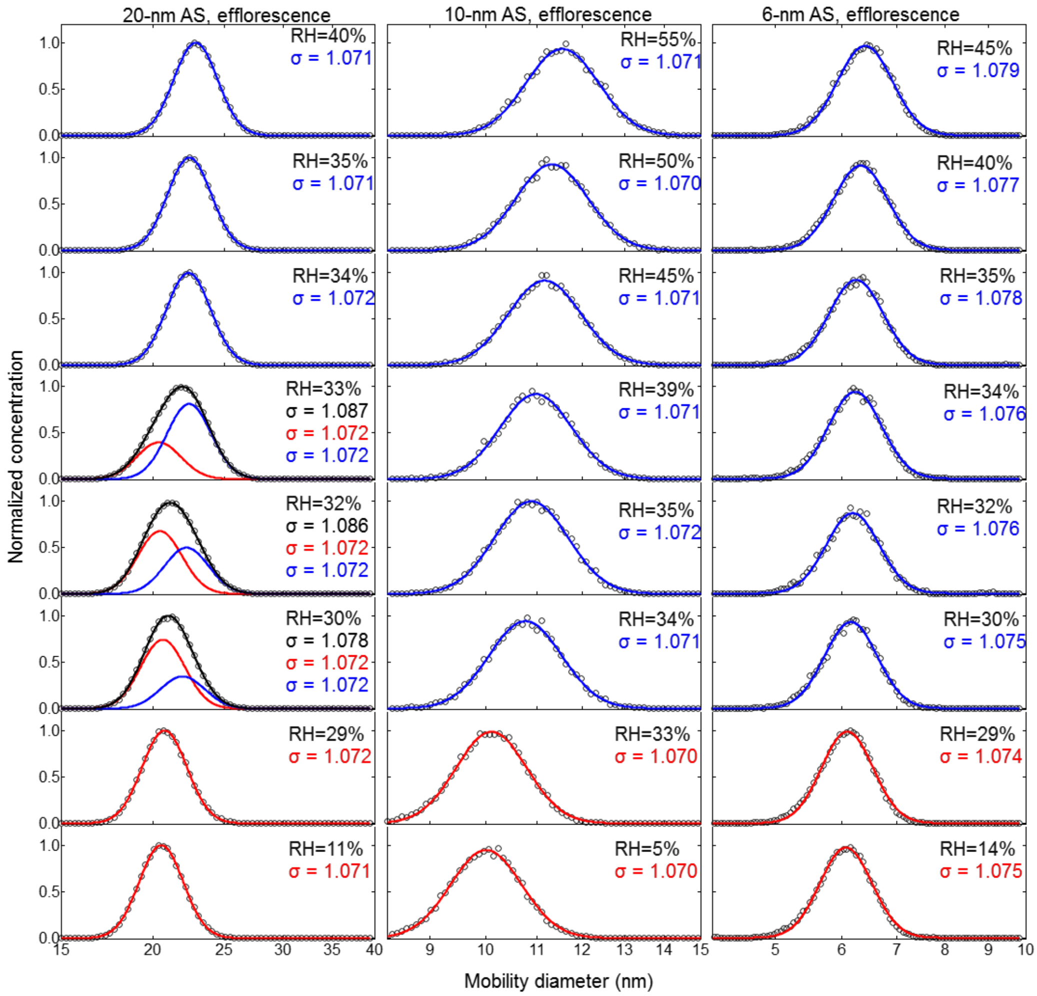


Figure 6. Efflorescence-mode measurements of ammonium sulfate (AS) aerosol nanoparticles with dry mobility diameter from 20-6nm. The measured (black circle) and fitted (solid lines) normalized size distribution are shown for increasing RH. The RH history in each measurement is 5%→97%→X%, where X is the RH value given in each panel.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

Atmospheric Measurement Techniques Discussions

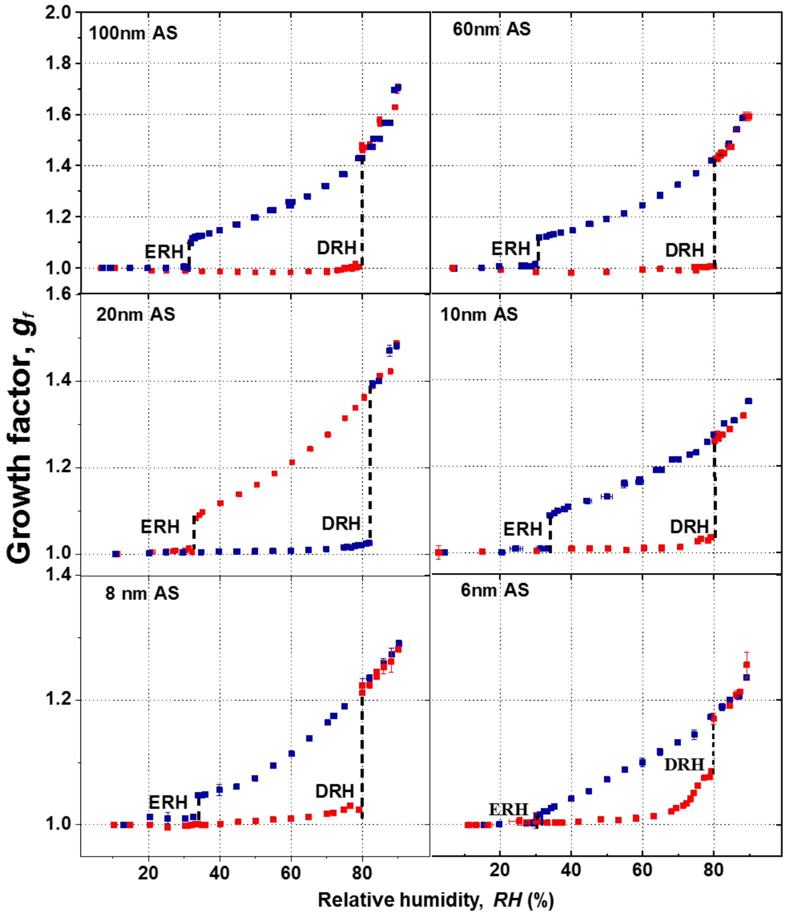


Figure 7. Mobility-diameter hygroscopic growth factors (g_f) of ammonium sulfate (AS) aerosol nanoparticles with dry mobility diameter from 6 to 100 nm in the deliquescence mode (red square and error bar) and the efflorescence mode (royal square and error bar). Deliquescence, and efflorescence relative humidity (DRH&ERH, black dashed line) of ammonium sulfate (AS) nanoparticles with dry mobility diameter from 6 to 100 nm.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

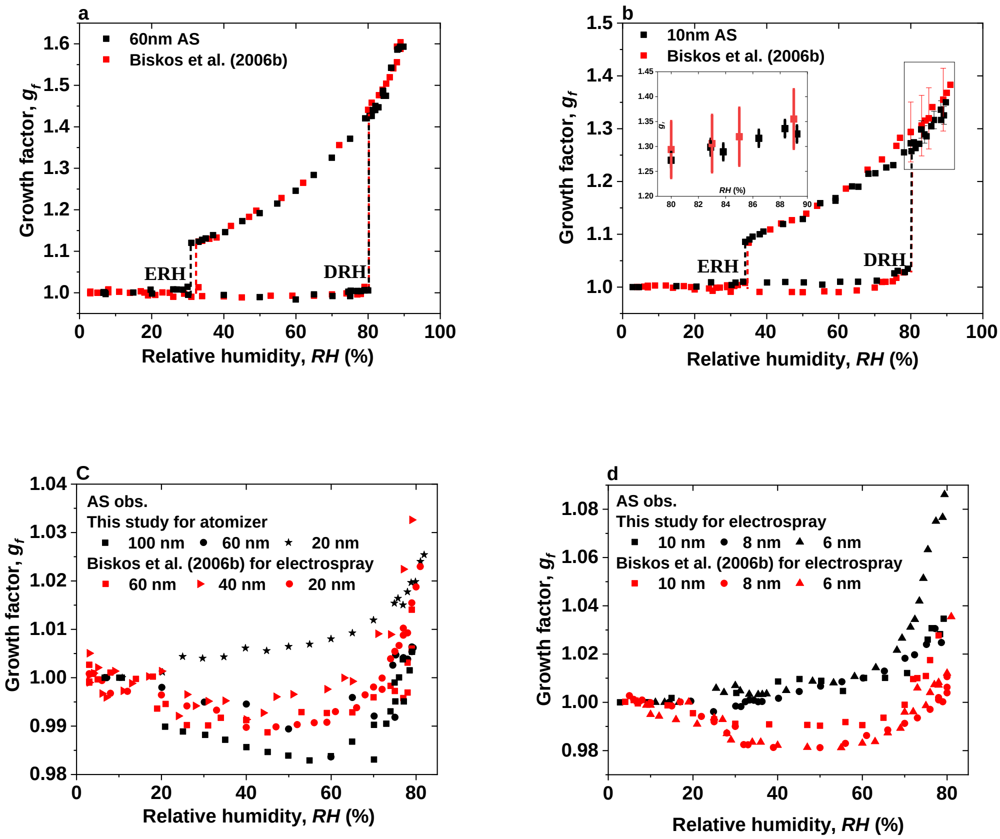


Figure 8. **(a-b)** Mobility-diameter hygroscopic growth factors (g_f, black squares), deliquescence and efflorescence relative humidity (DRH&ERH, black dashed lines) of ammonium sulfate (AS) nanoparticles with dry diameter 60 and 10 nm, respectively. Red squares and dashed lines show the respective results from Biskos et al. (2006b), respectively. Black and red uncertainties of growth factors at certain RH are calculated by $\sqrt{\left(\left(g_f\frac{\sqrt{2}\varepsilon_{Dp}}{D_p}\right)^2+\left(\varepsilon_{RH}\frac{dg_f}{dRH}\right)^2\right)}$, where ε_{Dp}, ε_{RH}, and g_f are uncertainty of particle mobility diameter, uncertainty of relative humidity, and growth factor with respect to RH, respectively (Mochida and Kawamura 2004). **(c-d)** Comparison of growth factors of ammonium sulfate (AS) nanoparticles with dry diameter range from 6 to 100 nm with Biskos et al. (2006b) prior to deliquescence of ammonium sulfate nanoparticles.

https://doi.org/10.5194/amt-2020-110
Preprint. Discussion started: 14 April 2020

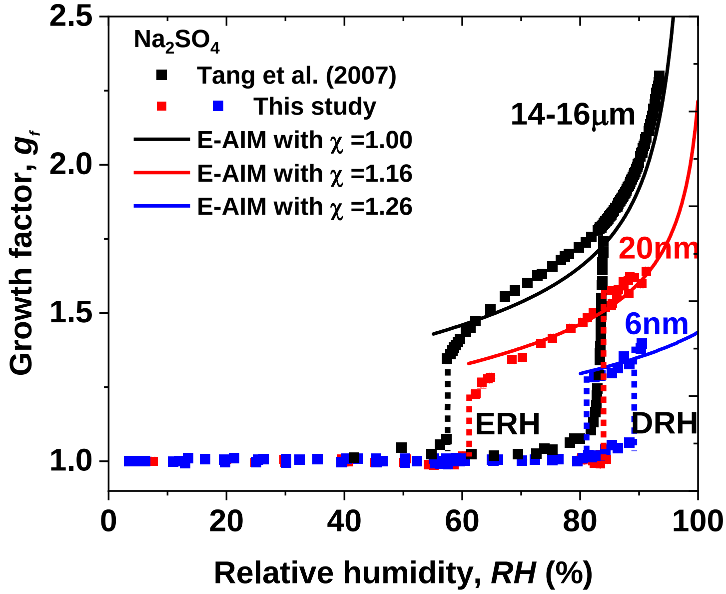


Figure 9. Mobility-diameter hygroscopic growth factors (g_f), deliquescence and efflorescence relative humidity (DRH&ERH, red and blue dashed lines) of sodium sulfate nanoparticles with dry diameter 20 (red square) and 6 (blue square) nm, respectively. Black squares and dashed lines show the respective results from Tang et al. (2007) with electrodynamic balance (EDB), respectively. In this study, the black, red, and blue curves show E-AIM predictions, including the Kelvin effect and shape factors (χ).