Design and Application of an Unattended Multifunctional H-TDMA System

HAOBO TAN,* HANBING XU,+ QILIN WAN,# FEI LI,# XUEJIAO DENG,# P. W. CHAN,@ DONG XIA,& AND YAN YIN**

* Key Laboratory for Atmospheric Physics and Environment, Nanjing University of Information Science and Technology, Nanjing, and Institute of Tropical and Marine Meteorology, China Meteorological Administration, Guangzhou, China
+ Sun Yat-sen University, Guangzhou, China
# Institute of Tropical and Marine Meteorology, China Meteorological Administration, Guangzhou, China
@ Hong Kong Observatory, Hong Kong, China
& Dongguan Meteorological Bureau, Dongguan, China
** Key Laboratory for Atmospheric Physics and Environment, Nanjing University of Information Science and Technology, Nanjing, China

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ABSTRACT

The hygroscopic properties of aerosols have a significant impact on aerosol particle number size distributions (PNSD), formation of cloud condensation nuclei, climate forcing, and atmospheric visibility, as well as human health. To allow for the observation of the hygroscopic growth of aerosols with long-term accuracy, an unattended multifunctional hygroscopicity-tandem differential mobility analyzer (H-TDMA) system was designed and built by the Institute of Tropical and Marine Meteorology (ITMM), China Meteorological Administration (CMA), in Guangzhou, China. The system is capable of measuring dry and wet PNSD, hygroscopic growth factor by particle size, and mixing states. This article describes in detail the working principles, components, and calibration methods of the system. Standard polystyrene latex (PSL) spheres with five different diameters were chosen to test the system's precision and accuracy of particle size measurement. Ammonium sulfate was used to test the hygroscopic response of the system for accurate growth factor measurement. The test results show that the deviation of the growth factor measured by the system is within a scope of $2^{0.01}$ to $2^{0.03}$ compared to Köhler theoretical curves. Results of temperature and humidity control performance tests indicate that the system is robust. An internal temperature gradient of less than 0.2 K for a second differential mobility analyzer (DMA2) makes it possible to reach a set-point relative humidity (RH) value of 90% and with a standard deviation of ±0.44%, sufficient for unattended field observation.

1. Introduction

Aerosol particles can impact the radiation balance of the earth’s atmosphere through scattering and absorption of solar radiation. They can also act as cloud condensation nuclei and alter the optical properties and life cycles of clouds and therefore indirectly impact the radiation balance of the earth’s atmosphere (Chylek and Coakley 1974; Twomey 1977). Aerosol hygroscopicity describes the interaction between aerosol particles and water vapor under specific vapor conditions and is determined by the physical and chemical properties of aerosols. Hygroscopic growth affects the optical properties of aerosols, the microphysical properties of clouds, and is a fundamental area of research in aerosol studies. The effects of aerosol hygroscopic growth can be divided into four major categories.

1) Alterations to the optical properties of particles, including particle number size distribution (PNSD) (Yoon and Kim 2006), phase function, and refractive index (Day et al. 2006; Tang and Munkelwitz 1994), which impact the direct radiative forcing of aerosols and cause further reductions in atmospheric visibility (Yoon and Kim 2006). Randall et al. (2007) used a GCM to predict changes in the aerosol size distribution and scattering coefficient caused by hygroscopic growth under varying relative humidity conditions and the relevant impact on the surrounding climate. They pointed out that a lack of understanding of
Aerosol hygroscopicity can lead to large inaccuracy in estimations of the direct climatic impact of aerosols.

2) Alterations to the properties of aerosols acted as cloud condensation nuclei. According to the Köhler theory (Köhler 1936), the formation of cloud droplets is dependent on the size and chemical composition of aerosol particles and the level of supersaturation. Some studies suggest that particle size plays a more important role than chemical composition in determining aerosols’ ability to nucleate cloud droplets (Deng et al. 2011; Dusek et al. 2006). Based on observation data from the past few decades, Hudson (2007) concluded that the cloud-nucleating ability of aerosol particles fluctuates substantially, and that the mixing state and the chemical composition (or the total mass) of hygroscopic matter also play important roles in affecting cloud-nucleating ability. At a given level of liquid water content, increases in concentration of cloud condensation nuclei (CCN) will result in a smaller effective radius for cloud droplets and higher cloud albedo, thus changing the life cycle of the cloud, creating indirect radiative effects and impacting the climate (Martinson et al. 1999).

3) The presence of an aqueous phase has an impact on heterogeneous chemical reactions and secondary aerosol formation, causing further changes in the concentration, PNSD, and chemical composition of atmospheric aerosols (Chameides and Stelson 1992).

4) Impacts on human health. Once inhaled into the human respiratory tract, aerosol particles will become deposited. The position and speed of this deposition are determined by the hygroscopicity of the aerosol particles. Some particles may deposit in the lungs, causing various diseases (Ferron et al. 1988; Schroeter et al. 2001).

Aerosol hygroscopicity is usually expressed by a growth function of the scattering coefficient [see Eq. (1), defined as \( f(RH) \)] or in terms of the hygroscopic growth factor [see Eq. (2), defined as \( Gf(RH) \)], which correspond to the two main methods of measurement:

\[
f(RH) = \frac{k_{sca}(RH)}{k_{sca}(dry)} \quad \text{and} \quad Gf(RH) = \frac{Dp(RH)}{Dp(dry)}. \tag{1}
\]

\[
Gf(RH) = \frac{k_{sca}(RH)}{k_{sca}(dry)} \quad \text{and} \quad Gf(RH) = \frac{Dp(RH)}{Dp(dry)}. \tag{2}
\]

In Eq. (1), \( k_{sca}(RH) \) and \( k_{sca}(dry) \) represent aerosol scattering coefficients at a given level of relative humidity and under dry conditions (usually, RH < 20%), respectively. In Eq. (2), \( Dp(RH) \) and \( Dp(dry) \) represent the diameters of an aerosol particle at a given level of relative humidity and under dry conditions, respectively. The scattering coefficient enhancement factor is a function of the chemical composition, hygroscopic growth factor, size, and shape of the aerosol particles. It is an important parameter in the calculation of direct radiative effects of aerosols and regional haze pollution (Day et al. 2006). Extensive research has been conducted both in China and abroad to observe \( f(RH) \) of aerosol particles using an integrating nephelometer in serial and parallel configurations, including the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) (Kim et al. 2006), the Tropospheric Aerosol Radiative Forcing Observational Experiment (TARFOX) (Kotchenruther et al. 1999), the Southern African Fire–Atmosphere Research Initiative (SAFARI 2000) (Magi and Hobbs 2003), the Indian Ocean Experiment (INDOEX) (Sheridan et al. 2002), the Smoke/Sulfates, Clouds, and Radiation in Brazil (SCAR-B) experiment (Kotchenruther and Hobbs 1998) and the Program of Regional Integrated Experiments on Air Quality over the Pearl River Delta in 2006 (PRIDE-PRD2006) (Liu et al. 2008). Liu and Zhang (2010) conclude from the results of these experiments that \( f(RH) \) is substantially higher in marine aerosols, moderate in urban and continental aerosols, and lowest in biomass burning aerosols (apparently related to the high carbon content in biomass combustion products).

The hygroscopic growth factor approach focuses more on changes in particle size and provides further information, including the proportion of soluble components and aerosol particle mixing state (see Fig. 1), which can be obtained by the hygroscopic-tandem differential mobility analyzer (H-TDMA). Figure 1 depicts the growth factor distributions that are expected for external and internal mixed aerosols (soot and salt). The H-TDMA instrument separates particles into groups of similar hygroscopic properties. Although this state of mixing strictly refers only to the hygroscopic properties, it nevertheless implies the extent of chemical mixing of the aerosol. However, it needs to be pointed out that externally mixed particles of similar hygroscopic growth cannot be separated using H-TDMA instruments.

In the past few decades, H-TDMA has been widely adopted across the world to measure hygroscopic growth factors. The H-TDMA system is based on the tandem differential mobility analyzer (TDMA) technique, which was first proposed by Liu et al. (1978) in 1978 for the purposes of measuring changes in particle diameter after treating the particles (humidification, drying, volatilization, chemical reaction, etc.). Rader and McMurry (1986) introduced the term TDMA, stating that the system can be used to measure particle size changes of 1%. TDMA has since been widely used in the measurement of size changes for various particles, for example, during humidification (H-TDMA), volatilization (V-TDMA) and reaction (R-TDMA). For more than two decades, H-TDMA has been employed globally in land- and ship-based surveys.
that measure aerosol hygroscopic growth factors. The regions observed include remote continental regions less affected by human activities, such as the northern forests of Europe (Petäjä et al. 2007), the European continent (Busch et al. 2002), high-Alpine sites in Europe (Sjogren et al. 2008), the tropical rain forest in Asia (Irwin et al. 2011), the midwestern United States (Carrico et al. 2005), and the Amazonian plains in South America (Rissler et al. 2004). Observational data for more polluted urban regions have been obtained in Europe (Adam et al. 2012; Baltensperger et al. 2002), the United States (Sakurai et al. 2005), and Asia (Chen et al. 2003; Liu et al. 2011; Meier et al. 2009; Mochida et al. 2006; Ye et al. 2011).

McMurry and Stolzenburg (1967) were the first to observe hygroscopicity in urban atmosphere aerosols. Trakumas et al. (1995) discovered that atmospheric aerosol hygroscopicity in Vilnius, Lithuania, was strongly seasonal with a Gf value between 1.25 and 1.60 during the summer, whereas most particles appear to be nonhygroscopic in the winter. Atmospheric aerosols in Taipei, Taiwan, feature both internal and external mixing modes. The compound (NH₄)₂SO₄ shows the highest abundance level, whereas organic compounds do not exert obvious effects (Chen et al. 2003). In Beijing, China, aerosols in the winter in terms of chemical composition are mainly carbonaceous aerosols and sulfates, and hygroscopicity is positively related to the air pollution index (Meier et al. 2009). According to data from the literature (Swietlicki et al. 2008), urban aerosols normally consist of nearly hydrophobic particles, less-hygroscopic particles, and more-hygroscopic particles. Nearly hydrophobic particles are found mainly in carbonaceous aerosol emissions from fossil fuel combustion, for example, automobile tailpipe emissions, which consist mainly of black charcoal and insoluble organic matters. In most cases, less-hygroscopic particles are the primary product of the aging of carbonaceous aerosols in the atmosphere, with air phase condensations being the key reactions accompanied by coagulations with other particles. The key elements are black charcoal, partially oxidized organic matter, and condensed inorganic salts. In the urban environment, the number fraction of nearly hydrophobic particles and less-hygroscopic particles drops as particle sizes increases, in accordance with that of the soot number size distribution from traffic emissions that peak at about 50–100 nm. More-hygroscopic particles are mainly composed of inorganic salts (e.g., sulfates and nitrates) with strong hygroscopic properties. Swietlicki et al. (2008) also did a fairly detailed review of H-TDMA observation activities before 2008. While H-TDMA is widely employed in aerosol hygroscopicity studies abroad, in China, only a few short-term observational projects have been carried out in Beijing (Meier et al. 2009), Tianjin (Liu et al. 2011), and Shanghai (Ye et al. 2011), and long-term systemic observations in heavily polluted areas are lacking.

In terms of observation technology, none of China’s domestic research institutions other than Fudan University (Ye et al. 2009) has reportedly set up an H-TDMA system on its own. This significantly hinders observations of surrounding aerosol hygroscopicity. At the same time, because of the extremely uneven temporal and spatial distribution of aerosol types, it is critical to collect data on aerosol hygroscopic changes in different regions of the country over a long period of time, which calls for even stricter requirements on the accuracy and stability of H-TDMA systems. Given the above conditions, the Guangzhou Institute of Tropical and Marine Meteorology (ITMM) under the China Meteorological Administration set up an unattended multifunctional H-TDMA system. The second section of this article describes the design of this H-TDMA system and its measurement functionality. Section 3 discusses the device’s calibration and the results of performance tests.

2. Design and application

The H-TDMA system mainly has seven components: (i) A bipolar neutralizer. This component exposes aerosol particles to high concentrations of bipolar radiative ions. See Wiedensohler (1988) for details regarding the charge distribution. (ii) A primary DMA (DMA1). The voltage of DMA1 is changed directly to select particles of a particular size. After this selection process, the particles exist in a monodispersed state, defined by both the width of the DMA transfer function and the fraction of particles containing multiple charges. (iii) A temperature and humidity control module, including a drier, a humidifier, and devices for measuring temperature and humidity. This
module monitors the temperature and humidity level throughout the system and ensures particles remain in a stable environment at the configured humidity level.

(iv) A second DMA (DMA2). This component separates and selects particles (under wet conditions) by size by using a scanning mobility particle sizer (SMPS). (v) A condensation particle counter (CPC) for counting the number of particles. (vi) Various accessory components. These components include a vacuum pump, which produces the suction necessary for aerosol sample collection and is placed at the end of the pipeline; an automated ball valve, which adjusts the direction of airflow; and an automated proportional valve, which adjusts the volume of the airflow. (vii) A software package that handles both system control and data collection simultaneously. See Fig. 2 for the design framework and Table 1 for a list of the main components.

Aside from ensuring reliable performance of all the components, the following measures have been taken so the system can also run under stable conditions over a long time frame: (i) A special design for the temperature and humidity control module featuring automatic feedback control of the humidifier so that it keeps working at the preset RH level for long periods of time. Fans are installed to achieve uniform temperature inside the outer casing. (ii) A closed circuit sheath flow is used in both DMA1 and DMA2. The humidification module humidifies the aerosol flow only and not the sheath flow.

Fig. 2. Framework of the H-TDMA system. Details of the various components of the system are found in section 2c.

**a. Control of temperature and humidity levels**

Stable temperature and humidity control is the most critical part of any H-TDMA system. This issue is discussed at length in the literature both in China and abroad. The approaches often adopted to deal with this issue include a water–air GORE-TEX pipe (Duplissy et al. 2008), a water–air Nafion membrane (Van Dingenen et al. 2005), an air–air Nafion membrane (Santarpia et al. 2004), and a mix of dry and wet air (Cubison et al. 2005; Weingartner et al. 2001). The system described in this article adopts the combination of air–air Nafion membrane and a mix of dry and wet air. The Nafion osmotic membrane features 18 Nafion polymerization pipes inside and a stainless steel casing on the outside. Osmotic movement occurs through the walls of the polymerization pipes in a direction determined by the vapor pressure difference between the air flows on both sides of the wall, that is, from the side of higher vapor pressure to the side of lower vapor pressure. When the system is in operation, the aerosol sample flow and the adjustment flow move in opposite directions across the walls of the polymerization pipes. The aerosol sample flow becomes humidified if the adjustment flow (wet) has a higher vapor pressure, and becomes dried otherwise. A water tank is required to produce a wet flow (see Fig. 2). After passing through the filter, clean air forms bubbles in the water tank. The air above the water level in the water tank has a relatively
This air is mixed with dry air (RH, 20%) in a proportion set by adjusting the proportional valve to create an adjustment flow for a specific RH level. This wet adjustment flow enters the space between the Nafion polymerization pipes (inside the stainless steel external casing), and moisture penetration between the adjustment flow and the aerosol sample flow begins. Once this continues for a certain amount of time, a relatively stable RH for the sample flow is reached. The volume of the adjustment flow can be controlled at a fixed level of 6.5 Lpm with a flow-limiting aperture. A proportional integral derivative (PID) control technology is adopted to improve adjustment efficiency and stability. It is worth noting that the direction of the osmotic penetration is determined by the vapor pressure of the flows and not the RH. Vapor pressure is a function of temperature and pressure. Where the pressures on both sides of the polymerization pipe walls are almost equal (both at approximately 1 atm), the higher the temperature, the higher the saturation vapor pressure. Therefore, when RH is set to a relatively high level (>85%), it is necessary to raise the temperature of the water as appropriate and to install a water trap before the high humidity adjustment flow passes through the Nafion pipes. This will avoid causing damage to the device as the flow cools down and enters the liquid phase. It is optimal for the water temperature to be 2°C–3°C higher than the temperature inside the apparatus housing, which can be achieved through repeated adjustments. Water temperature, temperature inside the apparatus housing, and the on–off state of the heater are automatically monitored and controlled by the software.

Temperature control is another important factor that affects measurement accuracy. Solutions that have often been adopted in the past include the use of a temperature control box (Ye et al. 2009), a water bath (Gysel et al. 2007; Weingartner et al. 2001), or placement in an air-conditioned room, where the temperature is kept constant (Johnson et al. 2008).

At high levels, RH is temperature sensitive and fluctuations in temperature may lead to an unstable RH. For instance, when the temperature is 20°C and RH is 90%, a change of 0.1 K can cause the RH to change by approximately 0.7%. Therefore, temperature control is very important for obtaining stable high RH levels in the H-TDMA system. As a matter of fact, irregular temperatures can affect RH levels in three ways. First, the water tank must be heated to prepare a wet flow at near saturation. Assuming the temperature of the water remains unchanged, a rapid change in temperature in the tank will make the wet flow less saturated, so a high RH is hard to achieve, or it causes the wet flow to become oversaturated and causes damage to the Nafion pipes as the flow cools down. Second, rapid changes in temperature can cause massive swings of sample flow RH levels and sheath flow RH levels in DMA2, making both difficult to stabilize. Third, the existence of a temperature gradient in DMA2 indicates that particles are in two different RH equilibrium states when entering and leaving DMA2, which will cause Gf values to be inaccurate. The first issue can be

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of component</th>
<th>Manufacturer</th>
<th>Model No.</th>
<th>Function</th>
<th>Quantity</th>
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</thead>
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<tr>
<td>1</td>
<td>Neutralizer</td>
<td>TSI</td>
<td>Kr85</td>
<td>Charging particles</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>DMA</td>
<td>TSI</td>
<td>3081L</td>
<td>Separating and selecting particles</td>
<td>2</td>
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<tr>
<td>3</td>
<td>CPC</td>
<td>TSI</td>
<td>3772</td>
<td>Counting of particle numbers</td>
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</tr>
<tr>
<td>4</td>
<td>Blowers</td>
<td>Microjammer</td>
<td>119494–00</td>
<td>Controlling sheath flow</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>Nafion tube</td>
<td>Perma Pure Inc.</td>
<td>PD-18T-24SS</td>
<td>Drying/humidifying of flow path</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>Mass flowmeter</td>
<td>Alicat Scientific</td>
<td>M-20LPM</td>
<td>Monitoring sheath flow</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>Vacuum pump</td>
<td>Wilson Co.</td>
<td>Thomas 2660CHI44</td>
<td>Providing flow suction</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>Temperature and humidity sensor</td>
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<td>HMP110 module</td>
<td>Measuring temperature and humidity level</td>
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<tr>
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<td>High-voltage power source</td>
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<td>10A12-p4-C</td>
<td>Powering DMA</td>
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<tr>
<td>11</td>
<td>Power amplifier</td>
<td>Vicor Power</td>
<td>VI-JW1-EX</td>
<td>Powering of blowers/automated valves</td>
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<td>Automated proportional valve</td>
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<td>24 V, 0.234&quot;, 202618</td>
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<td>EW29818–00</td>
<td>Filtering of sheath flow particles (nondrying)</td>
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<td>Supplying dry clean air for wet flow path/mixed flow path</td>
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<td>DAQ board</td>
<td>National Instruments Inc.</td>
<td>PCI-6034 PCI-6705</td>
<td>Acquiring data and control</td>
<td>2</td>
</tr>
</tbody>
</table>
solved by measuring the temperature of the casing and then matching the water temperature to that. Regarding the second and third issues, the use of a water bath or thermal cases can keep temperature fluctuations in the H-TDMA system within a very low limit (e.g., ±0.1°C). However, this involves some rather complex processes. The system discussed in this article is placed inside a nonthermal outer case and electric blowers are used to mix the air evenly inside the outer case. The entire apparatus is placed in an air-conditioned room at constant temperature, so that impact from external temperature changes is minimal. Temperature changes inside the case tend to be uniform.

b. Closed loop

A closed-loop design has been adopted for DMA1 and DMA2, meaning that sheath flow and excess flow are equal and in circular flow (see Fig. 2). A flowmeter is used to monitor and measure the volume flow. Calculations are made using the PID technology to determine the rotation speed of the blowers. A particle filter (filters only aerosol particles and not water vapor) is also connected. This design has an advantage over an open-loop design in that it keeps the system simple.

Because the range of particle sizes selectable by a DMA is determined by the sheath flow rate and the maximum voltage of the DMA, which is fixed under most conditions (10 kV with this system), the higher the sheath flow rate, the smaller the range of measurable particles. The accuracy of measurement and distinguishability of different particles is determined by the ratio between the sheath flow rate and the sample flow rate because of the transfer function, which is normally no less than 6:1. The higher the ratio, the more accurate the measurements are and the more distinguishable the particles are from each other. The rate of the sheath flow in the system described in this article is set to 6.5 Lpm (adjustable). The rate of the sample flow is set to 1 Lpm (also adjustable). The range of measurable particle sizes under this setting is 10–400 nm. In summary, all the above-mentioned factors interact with each other and work together to determine the range of measurable particle sizes and the corresponding accuracy of measurements.

Observations by Biskos et al. (2006) indicate that when the RH of a sheath flow and sample flow differ by more than 3%, significant inaccuracy can occur for Gf values of inorganic salts. The recommended RH difference between the two flows is under 2%. During the process of humidification, the RH of the sheath flow in the closed loop is determined by the flow rate of the sample flow. Humidity sensors are placed at both the entry and exit points for sample flows in DMA2 (T/RH_4 and T/RH_5 in Fig. 2) to measure aerosol humidity changes that have taken place inside DMA2. When the sheath flow and sample flow RH values reach equilibrium, the two sensors should show equal readings. Because the sheath flow rate is higher than in the sample flow (6.5:1), it acts as a buffer to add to the stability of the humidification process.

c. Measurement functionality and workflow

Conventional H-TDMA systems measure size-resolved Gf distributions primarily. The system discussed here is also capable of measuring dry and wet aerosol PNSD, and aerosol efflorescence. The following are the workflows for performing such measurements.

1) Gf distribution by particle size. The sample flow passes through the drier until RH falls <10%, and then it enters the neutralizer and DMA1 in succession. The selected particles pass through the humidifier_2 until its RH value reaches the preset value (e.g., RH = 90%). Then enter DMA2 in which particles (wet) are mobility-diameter selected according to the voltage. Finally, the resulting PNSD is determined with SMPS by the combination of downstream DMA2 and CPC. Aerosol deliquescence behavior can also be measured by this method with adjusting the preset RH of the humidifier.

2) Dry aerosol PNSD. A dry aerosol is passed through the drier, the neutralizer, DMA1, and CPC in succession to obtain the dry aerosol PNSD.

3) Wet aerosol PNSD. Wet aerosol is passed through the drier, the neutralizer, humidifier_1 (see Fig. 2), DMA1, and CPC in succession to obtain a wet aerosol PNSD. As has already been mentioned in section 2b, the normal measurement range of the system is 10–400 nm. Given that the distribution of aerosol particle size will necessarily spread and exceed the 400-nm limit after hygroscopic growth, one must lower the flow rate of aerosols in the circuit (e.g., to 0.3 Lpm), set the sheath flow at 3 Lpm, and increase the measurement range to up to around 1000 nm (sufficient for particles of under 400 nm before hygroscopic growth) when measuring wet aerosol PNSD. The measurements so obtained are very useful in the estimation of overall hygroscopic growth factor and aerosol extinction coefficient as well as the design of closure experiments investigating the optical properties of aerosols.

4) Aerosol efflorescence. Aerosols are passed through the drier, the neutralizer, the first humidifier_1, DMA1, humidifier_2 (see Fig. 2), DMA2, and CPC in succession to obtain the efflorescence curve of the aerosols. Following a single measurement at a fixed RH of 85% after humidifier_1, the relative humidity between the two DMAs in this instrument slowly decreases from
about 90% to 20% in humidifier_2. All or some of particles will exhibit efflorescence behavior (Santarpia et al. 2004).

In addition, taking the recommendation for H-TDMA design and construction into consideration (Duplissy et al. 2009), two key parameters in our H-TDMA system are as follows: (i) the sample RH are drier than 10% RH before entering the neutralizer and DMA1 and (ii) residence time is between 10 and 30 s depending on the flow rate of sample.

d. Data inversion

When the H-TDMA system is set to PNSD measurement mode, the SMPS method is the approach adopted for data inversion. Refer to Wang and Flagan (1990) for details of the data processing method. The main considerations here are multiple charge correction and diffusion loss correction.

When the system is set to Gf mode, there is no need for multiple charge correction or diffusion loss correction because it is the probability distribution of particle size after hygroscopic growth that is considered and not the absolute number of particles that have a particular particle size. Humidified aerosol flow is passed through DMA2 for scanning and CPC for recording. The measured Gf distribution function (MDF) is not equal to the Gf probability density function (PDF) because of the transfer function. To obtain an actual Gf PDF, a corrected data inversion approach is required. Two approaches are currently in common use. Using the TDMAfit method by Stolzenburg and McMurry (1988), one can effectively obtain the Gf distribution of particles having different levels of hygroscopicity through data inversion on the premise that all particles follow a Gaussian distribution and have different chemical compositions. During iterative computation, misconvergence of two particle types with similar hygroscopicity may occur and the assumed initial values may need to be adjusted. Stolzenburg and McMurry improved their algorithm in 2008 (Stolzenburg and McMurry 2008). Gysel et al. (2009) developed the TDMAinv method of data inversion, which treats Gf PDF as a piecewise linear function. It has the advantage of a high convergence rate even with interactive computation and is not reliant on initial values. Our system uses the TDMAfit method to fit the Gf PDF with a log-normal distribution. It achieves complete automation by programming features such as automatically adjusting initial values, detecting errors in fitting parameters, and correcting humidity [Eq. (18) in Keith and Arons 1954]. Figure 3 shows an example of Gf PDF and MDF for 110-nm ambient particles exposed at dry condition (RH < 10%) and at 90% RH.

e. Data acquisition and program control

The data acquisition and program control system for this H-TDMA is written with LabVIEW 8.5, a piece of virtual instrumentation software developed by National Instruments. Also in place is a data acquisition (DAQ) board. The original software’s source code is written by Collins (Collins et al. 2002). The current system, however, includes more functions, such as humidity level setting, a humidity stabilizing timer, a wet PNSD measuring sequence, and temperature control and feedback. The DAQ board is responsible for sampling analog signals, digital signals, and pulse signals coming from components of the system. It is also responsible for converting command signals coming from the computer into various electrical signals and sending them through to the control components. The software consists of three functional areas: user control, for setting the operational mode of the device and parameters; device status, for displaying the state and signals of all system components; and the data display area, where measurements obtained under various operational modes are displayed in graphs (see Fig. 4).

3. System calibration and performance test

a. System calibration

Calibration must be performed both before the H-TDMA system is in operation and after it has been in operation for a certain amount of time to ensure measurement accuracy. Calibration is done via the following steps.

1) DMA voltage calibration. When prompted by the program, the DAQ board transmits a voltage of 0–5 V
to the high-voltage transformer, which then transmits a high voltage (0–10 kV) to a DMA. Theoretically, the change should be linear throughout the full measurement range. However, considering the potential inaccuracy of the particle selection process, especially with smaller particle sizes, it is necessary to perform calibration in this respect. To do this, the equipment compares the actual voltages transmitted by the DAQ board and the high-voltage transformer using a high-precision multimeter that works out the values of the “slope” and “offset,” and enters them into the program.

2) Leak test and flow rate calibration. The length of the pipeline between the sample flow entry point and CPC is about 5 m. There are a number of converters and valves along the pipeline, and leaks along the pipeline may substantially interfere with measurements. To perform a leak test, the pipeline is divided into several sections and the flow rate at each section is measured. If the flow rates in all sections are equal or the difference is minimal, then the pipeline may be regarded as leak free. All the flow is calibrated by a standard flowmeter periodically.

3) Calibration of the temperature and humidity sensors. Temperature and humidity sensors are calibrated with a high-precision thermometer and dewpoint meter readings and enter the corresponding calibration factor into the program.

4) PID optimization of humidity control. This is to establish the relationship between the voltage on the control switch for the automated proportional valves and the humidity measurements through repeated testing. Incorporate that value into the PID control algorithm to achieve a stabilizing effect faster and to reduce the duration of the humidification process.

5) Pipeline length measurement. When the system is set to measure PNSD, pipeline length and flow rate determine the diffusion loss correction factor. Therefore,
an accurate measurement of the pipeline length is required. The length of the section between DMA1 and CPC must also be measured because the length of the section and the flow rate within determine the length of time it takes for particles to pass through the section, which has an effect on the SMPS outcome. While in SMPS mode, the system performs two scans, one with voltage going from low to high and the other with voltage going from high to low. If the distribution curves of the two scans match, then the length of the time it took the particles to pass through the section should be accurate.

6) Test of the hygroscopic growth factor of standard particle and inorganic salt particles. This will be explained in section 3b.

b. Results of performance tests

1) Tests with standard particles

The electronic mobility diameter of particles is measured by a DMA in the following manner: polystyrene latex (PSL) spheres (manufactured by TSI Co.) are mixed with superpure deionized water at a ratio of 1:1000. Using an aerosol generator (atomizer, TSI model 3076), a polydisperse sample aerosol is produced, which enters the H-TDMA through the flow entry point for measurement. This is repeated several times with each PSL particle size. If, according to the test results (Table 2), the mean particle sizes as measured by DMA1 are within the nominal sizes of PSL spheres, then the system is capable of selecting particles by electric mobility diameter with required accuracy. PSL spheres are not hygroscopic and theoretically their Gf value should be 1.0. With a target humidity level of 85%, the system produces a Gf very close to 1.0. This discrepancy is caused mainly by the nonlinearity in DMA voltage control and the difference between the two DMAs. The Gf value herein is recorded as the correction factor to be applied in future measurements.

2) Humidograms of pure ammonium sulfate

The hygroscopic growth curve of pure inorganic salt particles can be explained fairly adequately by the Köhler curve (Köhler 1936) and the physical and chemical properties of the inorganic components of the salt. Tang and Munkelwitz (1993, 1994) give the hygroscopic growth curve and parametric fitting formula of common inorganic salts on the basis of electronic dynamic balance (EDB). A substantial amount of laboratory work was done in the past to measure the hygroscopicity of inorganic salts and soluble organic compounds. These measurements can be applied to a thermodynamic model based on mole fractions in order to work out the water content of particles. They can also be used to test the H-TDMA system. Pure ammonium sulfate has well-observed hygroscopic properties and was therefore chosen for the test. Ammonium sulfate was mixed with superpure deionized water at a ratio of 1:1000. An aerosol generator (TSI model 3076) was then used to produce a polydisperse aerosol that entered the H-TDMA through its flow entry point. Gf as RH changes were then measured. See Fig. 5 for test results.

The solid triangles in Fig. 5 represent Gf values of 100 nm of ammonium sulfate aerosol at varying RH values. The solid line is the Gf curve corresponding to Tang’s calculation (Tang and Munkelwitz 1994). Gf measurements were processed as valid data only if, during the DMA2 scan, the difference between the RH at the exit point (T/RH_4 in Fig. 2) of DMA2 and the preset value exceeded 1%, and if the difference between the RH values at the entry and exit points (T/RH_4 and T/RH_5 in Fig. 2) of DMA2 do not exceed 1% (i.e., equilibrium of sheath and sample flows). When RH ≤ 78%, the Gf value stays mostly in the vicinity of 1.0 and changes are rather insignificant. When RH ≥ 79%, the value of Gf surges, from 1.43 (RH = 79%) to 1.53 (RH = 85%) to around 1.71 (RH = 90%). The deliquescence point of \( \text{NH}_4\text{SO}_4 \) aerosol was 80% ± 2% when Badger et al. conducted hygroscopic tests on 50- and 100-nm \( \text{NH}_4\text{SO}_4 \) aerosols at the temperature of 15°C (Badger

Table 2. Results of tests using standard particles.

<table>
<thead>
<tr>
<th>Nominal sizes of PSL spheres (nm)</th>
<th>Mean particle size (nm)</th>
<th>Gf (correction factor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 ± 1</td>
<td>0</td>
<td>1.01 ± 0.006</td>
</tr>
<tr>
<td>80 ± 3</td>
<td>83</td>
<td>1.01 ± 0.005</td>
</tr>
<tr>
<td>151 ± 4</td>
<td>150</td>
<td>1.01 ± 0.008</td>
</tr>
<tr>
<td>240 ± 5</td>
<td>236.5</td>
<td>0.99 ± 0.01</td>
</tr>
</tbody>
</table>

Fig. 5. Humidogram of ammonium sulfate for 100-nm particles. Solid line describes the deliquescence water uptake at increasing RH. Vertical line is the deliquescence point.
et al. 2006). When Brooks et al. (2004) conducted tests on (NH$_4$)$_2$SO$_4$ aerosols of varying particle sizes at the temperature of 30°C, the deliquescence point observed was 77% ± 2%. The deliquescence point in our case was 28°C, giving a deliquescence point of 79% ± 2%, somewhere between that of the two tests mentioned above. Deliquescence happens very quickly. For submicron ammonium sulfate particles, it is usually a matter of a few milliseconds. According to Biskos et al. (2006), if the mean appears somewhere around the deliquescence point, then it is because the difference between the RH levels of the sample and sheath flows exceeds 3%, which results in an excessively high RH gradient between the entry and exit points of DMA2 and leaves the particles in an unstable state while inside DMA2. The test results in Fig. 5 show that the particles were in a stable state when the test was conducted, suggesting that a humidified system can afford more stable test conditions. Furthermore, the Gf values obtained from this H-TDMA system during RH scans match rather well with theoretical projections, having deviating only −0.01 to −0.03 (about 2% lower). Taking into account measurement inaccuracies of the humidity sensors, the Gf measurements are well fitted to the theoretical curve.

3) TEMPERATURE AND HUMIDITY CONTROL STABILITY TESTING

How effectively temperature and humidity are controlled within the H-TDMA system determines the level of accuracy and repeatability of measurements, particularly so in the case of unattended field observation stations. The system was placed in an air-conditioned room with a temperature of 25°C at the time of the test. The temperature inside the case of the H-TDMA system was higher than the preset temperature on the air conditioner. There was a slow process of heat exchange and equilibrium between the inside of the case and the external environment. The extent of the temperature change inside the case was smaller than that of the room. Figure 6a shows the temperature records for one day. Changes in outdoor temperature (green line of circles) ranged from 10°C to 20°C and the room temperature (red dash line) was between 24°C and 26°C. Note that T_4 and T_5 each represent the temperature before and after DMA2. The changes in both are very consistent with a difference of less than 0.2 K. This minor difference can be attributed to the heat generated by the blower. The results show that particles, after reaching hygroscopic equilibrium, do not undergo a substantial RH change because of temperature changes in DMA2, which ensures a stable measurement process. Figure 6b shows the RH test results. The system was set to H-TDMA mode at the time of the test, with a target humidity level of 90%. From the diagram, RH_1 (after the drier) was kept under 10% to ensure aerosol particles were dry. RH_4 and RH_5 (humidity level before and after DMA2, respectively) both stayed in the vicinity of 90% with a standard deviation of ±0.44%, which means the system performed as well as the H-TDMA systems of many research institutions abroad (Duplissy et al. 2009). Humidity levels were stable inside DMA2, including in the closed sheath flow loop and hardly interfered with Gf measurements. Conditions for taking H-TDMA measurements were met.

4) COMPARISON OF SMPS MODE WITH A COMMERCIAL INSTRUMENT

A number of types of commercial equipment are available for measuring PNSD. Watson et al. (2011) made a comparison between four types that are commonly used around the world: the TSI Nano, TSI standard, Grimm...
(Model: SMPS + C), and MSP Wide-Range Particle Spectrometer (WPS). They concluded that the two models by TSI gave consistent measurements in the 10–80-nm particle size range, the Grimm is in the 10–30-nm range, and the TSI standard gives similar results in the 30–200-nm range. The causes for the inaccuracy may include charge efficiency, CPC efficiency, etc. Overall, model 3936 by TSI provides superior accuracy. The H-TDMA system discussed in this article has an additional particle size spectrum scan function, as it uses the same model of SMPS, model 3936. Comparison tests were performed to ascertain the accuracy of the system measuring PNSD. Figure 7 shows the results of five synchronized tests conducted on 9 November 2011. The data shown are the average of the results from five tests. In the 50–400-nm particle size range, the results from both systems were very close. Differences were more notable in the 10–50-nm range, yet still within ±10% of each other. Causes for the differences include (i) differing levels of diffusion loss compensation—the smaller the particle size, the higher the compensation factor, and the greater the inaccuracy of a valid particle count; (ii) different intervals between scans; and (iii) each of the two systems uses its own CPC to perform a count, and how the CPCs were calibrated could have contributed to the differences in the results.

4. Conclusions

This article describes the design and application of an H-TDMA system set up by the Institute of Tropical and Marine Meteorology, CMA, in Guangzhou. The system features automatic feedback temperature and humidity control, internal air exchange (inside the outer casing), and a closed loop of sheath flow to enable stable and intelligent operation. Results of temperature and humidity control performance testing show that when RH = 90%, the standard deviation of RH is ±0.44%, indicating that the system is running in a highly stable state and meets the requirements for long-term unattended field observation tasks. Results of tests with standard PSL spheres and ammonium sulfate particles and a subsequent comparison with a TSI 3969 show that the H-TDMA system is capable of measuring PNSD accurately, as well as Gf, with measurement results generally matching the Köhler curve with a deviation of −0.01 to −0.03. The incorporation of wet particle size distribution and particle efflorescence measurement functions can widen the application of the system in terms of the valuable data it can produce.

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