Technical note: Measurement of chemically-resolved volume equivalent diameter and effective density of particles by AAC-SPAMS

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Abstract

Size and effective density (ρ_e) are important properties of aerosol particles and are related to their influences on human health and the global climate. The volume equivalent diameter (D_{ve}) is an intrinsic property that is used to evaluate particle size. ρ_e, defined as the ratio of particle density to a dynamic shape factor (χ), is used to characterize the physical property of a particle as an alternative to particle density. However, it is still challenging to simultaneously characterize the D_{ve} and ρ_e of particles. Here, we present a novel system that classifying particles with their aerodynamic diameter (D_a) by aerodynamic aerosol classifiers (AAC) and determining their vacuum aerodynamic diameter (D_{va}) by single particle aerosol mass spectrometry (SPAMS) to achieve a measurement of D_{ve} and ρ_e. The reliability of the AAC-SPAMS system for accurately obtaining D_{ve} and ρ_e is verified based on the results that the deviation between the measured values and the theoretical values is less than 6% for the size-resolved spherical polystyrene latex (PSL). The AAC-SPAMS system is applied to characterize the D_{ve} and ρ_e of $(NH_4)_2SO_4$ and $NaNO_3$ particles, suggesting that these particles are aspherical and their ρ_e are independent of particle size. Finally, the AAC-SPAMS system is deployed in a field measurement, showing that it is a powerful technique to characterize the chemically-resolved D_{ve} and ρ_e of particles in real time.

1. Introduction

Size and particle density (ρ_p) are critical parameters of aerosol particles in quantifying the impact of aerosols on air quality, human health and global climate change (Buseck and Posfai, 1999; Poschl, 2005; Pitz et al., 2003). Effective density (ρ_e) has been adopted to characterize the physical property of a particle as an alternative to ρ_p, since ρ_p for aspherical aerosol particles is hardly measured (Sumlin et al., 2018; Katrib et al., 2005). Size and ρ_e govern the transport properties of a particle both in the atmosphere and in the human respiratory system (Seinfeld and Pandis, 1998; Liu and Daum, 2008) and directly/indirectly influence the potential of the particle to absorb or reflect solar radiation (Tang, 1997; Zhao et al., 2019; Liu and Daum, 2008). ρ_e can also provide information concerning particle morphology (Yon et al., 2015) and serve as a tracer for atmospheric processing (Guo et al., 2014; Yin et al., 2015; Liu et al., 2015). However, the quantitative relationship between aerosol properties, namely, size and ρ_e, and their effects on air quality, human health and global climate change is not yet well understood, which is partly because important aerosol properties cannot be measured by current techniques.

Size. Size is a fundamental property of particles, which can be parameterized by the physical quantity of volume equivalent diameter (D_{ve}). Defined as the diameter of a spherical particle with the same volume as the particle (DeCarlo et al., 2004), D_{ve} is an intrinsic physical quantity that can be used to evaluate the actual size of the particle. However, to date, atmospheric science usually describes particle size by other diameter definitions, such as the electric mobility diameter (D_m), aerodynamic equivalent

diameter (D_a) and vacuum aerodynamic equivalent diameter (D_{va}), whose relationships with D_{ve} are shown in Eqs. (1)-(3), respectively:

$$\frac{D_m}{C_c(D_m)} = \frac{D_{ve}}{C_c(D_{ve})}\chi_t, \quad (1)$$

$$D_a = D_{ve}\sqrt{\frac{\rho_p C_c(D_{ve})}{\chi_t \cdot \rho_0 \cdot C_c(D_a)}}, \quad (2)$$

$$D_{va} = \frac{\rho_p}{\rho_0}\frac{D_{ve}}{\chi_v}, \quad (3)$$

where $C_c(D)$ is the Cunningham slip correction factor, χ_t and χ_v represent the aerosol dynamic shape factor (χ) in the transition regime and in the free-molecule regime, respectively, and ρ_0 represents the unit density of 1.0 g/cm^3. From the definitions, it can be seen that D_m, D_a, and D_{va} are originally derived from D_{ve}, but in actuality, they do not reflect the actual size of the particle. Meanwhile, D_{ve} cannot be easily obtained, which limits its application in the scientific community.

Effective density. At present, three definitions of ρ_e are introduced in atmospheric science (DeCarlo et al., 2004): the first definition (ρ_e^I) is the ratio of the measured particle mass (m_p) to the particle volume (V) calculated assuming a spherical particle with a diameter equal to the measured D_m; the second definition (ρ_e^{II}) is the ratio of ρ to χ (Hand and Kreidenweis, 2002); and the third definition (ρ_e^{III}) is the ratio of D_m and D_{va}, all of which are expressed in Eqs. (4)-(6), respectively.

$$\rho_e^I = \frac{6m_p}{\pi {D_m}^3} \quad (4)$$

$$\rho_e^{II} = \frac{\rho_p}{\chi} \quad (5)$$

$$\rho_e^{III} = \frac{D_{va}}{D_m}\rho_0 \quad (6)$$

The definitions of ρ_e^I and ρ_e^{III} can be derived into the final forms, as shown in the Eqs.(7) and (8), respectively.

$$\rho_e^{\mathrm{I}} = \frac{\rho}{\chi t^3} \cdot \left(\frac{C_c(D_{ve})}{C_c(D_m)}\right)^3 \quad (7)$$

$$\rho_e^{III} = \rho \cdot \frac{C_c(D_{ve})}{\chi^2 \cdot C_c(D_m)} \quad (8)$$

The Eq. (7) is derived from combining the Eq. (1) with Eq. (4) in which m_p is equal to 1/6 $\rho \cdot D_{ve}^3$. The detailed derivation of Eq. (8) was presented in Schneider et al. (2006). A variety of methods are developed to characterize ρ_e^I and ρ_e^{III}, among which the more advanced methods are to achieve the measurement of the chemically-resolved effective density. Combining a single particle soot photometer (SP2) with a (volatility) tandem differential mobility analyser ((VT)DMA) can measure the ρ_e^I of particles mixed with soot (Zhang et al., 2016b; Wu et al., 2019; Han et al., 2019). The measurement of chemically-resolved ρ_e^{III} can be achieved by coupling a DMA with an on-line aerosol mass spectrometer including the single particle laser ablation time-of-flight mass spectrometer (SPLAT I/II) (Zelenyuk et al., 2005; Zelenyuk et al., 2006; Alexander et al., 2016), aerosol mass spectrometer (AMS) (Dinar et al., 2006; Schneider et al., 2006; Kiselev et al., 2010), aerosol time-of-flight mass spectrometer (ATOFMS) (Spencer and Prather, 2006; Spencer et al., 2007), and single-particle aerosol mass spectrometry (SPAMS) (Zhang et al., 2016a; Zhai et al., 2017). However, the ρ_e^I and ρ_e^{III} are demonstrated to have the inherent characteristics of decreasing with increasing particle size (Eqs. (7) and (8)) in a separate paper. Therefore, it will introduce systemic error when assessing the particle impacts on visibility, human health and climate from the physical quantities in ρ_e^I and ρ_e^{III}. In contrast, ρ_e^{II} is independent of particle size. Previously, ρ_e^{II} and the real part in the refractive index (n) can be retrieved from a fitting procedure that compares the measured light-scattering intensity of particles (R_{meas}) to

101 the theoretical values ($R_{theory,test}$) calculated by a series of n and ρ_e^{II} values. Moffet and
102 Prather (2005) successfully obtained ρ_e^{II} for spherical particles by single particle mass
103 spectrometry. However, subject to the accuracy of Mie theory for the aspherical
104 particles, dry NaCl and calcium-rich dust particles were failed to fit the $R_{theory,test}$ well
105 to R_{meas} (Moffet et al., 2008). Similarly, Zhang et al. (2016a) failed to simultaneously
106 retrieve ρ_e^{II} and n for $(NH_4)_2SO_4$ and $NaNO_3$ particles. To our best knowledge, there is
107 no effective technique to achieve the measurement of ρ_e^{II} for aspherical particles. For
108 reference, the symbol ρ_e in the following text refers to the definition of ρ_e^{II}.
109 The aim of the present work is to develop a method to simultaneously obtain D_{ve} and
110 ρ_e. The established system of an aerodynamic aerosol classifier (AAC)-SPAMS is
111 capable of characterizing the D_a and D_{va} of particles, which can be applied to
112 theoretically derive D_{ve} and ρ_e. To verify the reliability of the AAC-SPAMS system, we
113 apply it to measure the D_{ve} and ρ_e of the spherical particles of polystyrene latex (PSL).
114 The results are in good agreement with the theoretical values. Finally, the AAC-SPAMS
115 system is applied to measure the D_{ve} and ρ_e for $(NH_4)_2SO_4$ and $NaNO_3$ particles and for
116 the chemically-resolved atmospheric particles.
117
118 **2. Experimental section**
119 **2.1 Measurement system**
120 Figure 1 shows a schematic diagram of the AAC-SPAMS system. The particles are
121 first dried by a diffusion drying tube (TSI 9302, USA), classified by AAC (Cambustion
122 Ltd., UK) based on the aerodynamic diameters D_a, and then transported into SPAMS in

which the D_{va} and the mass spectra of individual particles are obtained. The working principle of the AAC is described in detail elsewhere (Tavakoli and Olfert, 2013). AAC consists of two coaxial cylinders that rotate at the same rotational speed. Polydisperse particles enter into the space between the cylinders (i.e., classification column) and experience a centrifugal force that causes them to move toward the outer cylinder. The particles to be classified can leave the classification column with the particle-free sheath flow and finally exit the AAC with the sample flow. Thus, the D_a values of classified particles can be derived from their relationship with their relaxation time (τ), as shown in Eq. (9):

$$\tau = \frac{C_C(D_a)\cdot\rho_0\cdot {D_a}^2}{18\mu} \quad (9)$$

where μ is the gas dynamic viscosity. Particles with large relaxation times impact and adhere to the outer cylinder, while particles with small relaxation times exit the classifier with the exhaust flow. The exhaust flow from the AAC was about 0.3 lpm, and the Size Resolution Parameter (Rs) of the AAC was set as 40.

Detailed information about the operation of SPAMS (Hexin Analytical Instrument Co., Ltd., China) is described elsewhere (Li et al., 2011). Briefly, the particles are introduced into the vacuum system through a 0.1 mm critical orifice and are gradually collimated into a beam in the aerodynamic lens. Two continuous diode Nd:YAG laser beams (532 nm) are used to aerodynamically size the particles, which are subsequently desorbed/ionized by a pulsed laser (266 nm) that is triggered based on the velocity of a specific particle. The generated positive and negative ions are recorded with the corresponding particle size. The D_{va} of the particle is related to the transit time between

the two laser beams (532 nm) in SPAMS, which can be obtained by using a calibration curve generated from the measured transit times of a PSL series with predefined sizes (nominal diameters).

2.2 Laboratory experiments

Dried spherical PSL (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto) (ρ_p = 1.055 g/cm^3 and χ = 1.0) with D_{ve} values of 203 ± 5 nm, 310 ± 6 nm, 510 ± 5 nm, and 740 ± 6 nm were used in the AAC-SPAMS system, and the D_{ve} was verified by Scanning Mobility Particles Sizer (Model 3938, TSI Inc., USA). The PSL particles were first classified by AAC, and then their D_{va} values were obtained by SPAMS. ACC-SPAMS was also applied to the particles of $(NH_4)_2SO_4$ (ρ_p = 1.77 g/cm^3) and $NaNO_3$ (ρ_p = 2.26 g/cm^3) with D_a values of 250.0 nm, 350.0 nm, 450.0 nm and 550.0 nm. Besides, to present the measurement uncertainty of the AAC, the D_a values of these PSL particles were measured to be 212.8 ± 0.2, 324.7 ± 0.4, 529.9 ± 0.4, and 767.5 ± 0.4, respectively, by the system of AAC- condensation particle counter (CPC), which shows that the AAC has the deviations of 1.1%, 1.3%, 0.8%, and 0.7% for determining the D_a values of the particles.

2.3 Ambient sampling

For field observations, the AAC-SPAMS system was placed in science and technology enterprise accelerator A2 Block, Guangzhou, China, to characterize the D_{ve}, ρ_e and chemical compositions of aerosol particles. The sampling inlet was hung 2.5 meters from the third floor (~12 m above ground level). Ambient aerosol particles were

167 introduced into the AAC through a 5 m long conductive silicone tube with an inner
168 diameter of 6 mm and a $PM_{2.5}$ cyclone inlet. The sampling flow from the $PM_{2.5}$ cyclone
169 inlet was 3 lpm, and the residence time in the conductive silicone tube was
170 approximately 5 seconds. Sampled particles were classified by the AAC as one of four
171 D_a: 250.0 nm, 350.0 nm, 450.0 nm and 550.0 nm. The sampling time for the particles
172 of each D_a was approximately 10 minutes. From July 6th to 8th, 2019, approximately
173 129,869 ionized particles were obtained from nine rounds of measurement. The
174 sampling details are shown in Table S1. The number of ionized particles with the D_a of
175 250.0, 350.0, 450.0, and 550.0 nm is about 35,609, 38,374, 31,910, and 23,976,
176 respectively. The sampled ~100,000 particles are first classified by using an adaptive
177 resonance theory neural network (ART-2a) (Song et al., 1999) with a vigilance factor
178 of 0.75, a learning rate of 0.05 and 20 iterations.
179

180 **2.4 Theoretical derivation of D_{ve} and ρ_e from D_a and D_{va}**

181 D_{ve} is the accurate physical quantity of the size of a particle. ρ_e is an alternative
182 property for ρ_p, which is consistent with the property of ρ_p in terms of being independent
183 of particle size. These two properties cannot yet be simultaneously measured for
184 unknown particles by current techniques. In this study, the calculations of D_{ve} and ρ_e for
185 unknown particles are theoretically derived from D_a and D_{va}. Combining Eqs. (2) and
186 (3), we obtain the following Eq. (10):

187 $$C_c(D_a)\frac{{D_a}^2}{D_{va}} = D_{ve}C_c(D_{ve})\frac{\chi_v}{\chi_t} \quad (10)$$

188 Based on the approximation between χ_v and χ_t ($\chi_v \approx \chi_t = \chi_a$) (DeCarlo et al., 2004), Eq.

189 (10) becomes Eq. (11):

190 $$C_c(D_a)\frac{{D_a}^2}{D_{va}} = D_{ve}C_c(D_{ve}) \quad (11)$$

191 The Cunningham Slip Correction Factor is calculated by Eq. (12) (DeCarlo et al., 2004):

192 $$C_c(D) = 1 + \frac{\lambda}{D}\left(A + B \cdot \exp\left(\frac{C \cdot D}{\lambda}\right)\right), \quad (12)$$

193 where λ is the mean free path of the gas molecules, and *A*, *B* and *C* are empirically
194 determined constants specific to the analysis system. The values of *A*, *B* and *C* are 2.33,
195 0.966, and -0.498, respectively, which are provided by the manual of the AAC.
196 Substituting Eq. (12) into Eq. (11) obtains the Eq. (13).

197 $$\frac{{D_a}^2}{D_{va}} + \frac{D_a \cdot \lambda}{D_{va}}\left(A + B \cdot \exp\left(\frac{C \cdot D_a}{\lambda}\right)\right) = D_{ve} + \lambda\left(A + B \cdot \exp\left(\frac{C \cdot D_{ve}}{\lambda}\right)\right) \quad (13)$$

198 Thus, if the D_a and D_{va} of an unknown particle can be measured, its D_{ve} will be
199 calculated according to Eq. (13). Finally, the ρ_e value of the particles is calculated by
200 the D_{va} and D_{ve} values according to Eq. (14), which is obtained by combining Eq.(3)
201 and Eq.(5):

202 $$\rho_e = \frac{\rho_p}{\chi_a} = \frac{D_{va}}{\rho_0 \cdot D_{ve}} \quad (14)$$

203 Thus, we can obtain both the D_{ve} and ρ_e values of unknown particles based on the D_a
204 and D_{va} values. Because the AAC and SPAMS instruments have the ability to determine
205 D_a and D_{va}, the AAC-SPAMS system, which is developed in this study, can be used to
206 obtain the D_{ve} and ρ_e values for unknown particles.

207

208 ## 3. Results and discussion

209 ### 3.1 Verification of the AAC-SPAMS system to obtain D_{ve} and ρ_e

210 The D_{va} distribution of PSL particles with predefined D_{ve} values after screening by

the AAC is shown in Figure S1. We used Gaussian fitting to obtain the peak D_{va} for PSL particles of predefined size with an R-squared fitting coefficient (R^2) over 0.98. Each fitting has a full width at half maximum (FWHM) of 6.6%, 4.4%, 2.3% and 2.2%, and the corresponding peaks are 215.8 nm, 319.0 nm, 532.1 nm and 803.5 nm, respectively. Substituting the D_a and D_{va} values of PSL into Eq. (11), the measured D_{ve} ($D_{ve,me}$) of PSL from AAC-SPAMS system is 203.6 nm, 309.7 nm, 511.6 nm and 737.2 nm, respectively (Figure 2a). Thus, the deviations between the theoretical D_{ve} ($D_{ve,th}$) and $D_{ve,me}$ values are 0.3%, -0.1%, 0.3% and -0.4%, respectively. On the other hand, the measured ρ_e ($\rho_{e,me}$) values of the particles are calculated from the D_{va} and $D_{ve,me}$ values with Eq. (14), and the $\rho_{e,me}$ values are 1.1 g/cm^3, 1.0 g/cm^3, 1.0 g/cm^3, and 1.1 g/cm^3 (Figure 2b). The deviations of $\rho_{e,me}$ are determined to be 4.3%, -5.2%, -5.2%, and 4.3%, respectively, by comparing to the theoretical ρ_e ($\rho_{e,th}$) that is equals to the ρ_p for the spherical particles (i.e. 1.055 g/cm^3 of PSL particles). That is, the deviations of $D_{ve,me}$ and $\rho_{e,me}$ characterized by the AAC-SPAMS system are within 1% and 6%, respectively. We therefore conclude that the AAC-SPAMS system is highly accurate for obtaining aerosol D_{ve} and ρ_e.

3.2 Application of the AAC-SPAMS system for obtaining D_{ve} and ρ_e of $(NH_4)_2SO_4$ and $NaNO_3$

Figure S2 shows the D_{va} distributions of $(NH_4)_2SO_4$ and $NaNO_3$ particles, which have D_a values of 250.0, 350.0, 450.0, and 550.0 nm, as screened by the AAC. The D_{va} peaks are obtained by Gaussian fitting, with R^2 values over 0.93 and FWHM values ranging

233 from 7.6% to 10.6%. The $(NH_4)_2SO_4$ particles have D_{va} values of 300.0, 418.0, 551.1,
234 and 695.1 nm (Figure S2), which correspond to particles possessing $D_{ve,me}$ values of
235 177.3, 254.4, 331.8, and 409.3 nm, respectively, according to Eq. (11). Substituting the
236 values of D_{va} and $D_{ve,me}$ into Eq. (12), the $\rho_{e,me}$ values are 1.7, 1.6, 1.6, and 1.7 g/cm^3
237 (Figure 3a), respectively. Similarly, the selected $NaNO_3$ particles are determined to
238 have D_{va} values of 321.0, 454.9, 599.8, and 755.3 nm (Figure S2), corresponding to
239 $D_{ve,me}$ values of 150.1, 218.2, 287.0, and 355.9 nm, respectively. The $\rho_{e,me}$ values of the
240 $NaNO_3$ particles are 2.2, 2.0, 2.0, and 2.1 g/cm^3 for the four particle sizes (Figure 3b),
241 respectively. Figure 3 also shows that the $\rho_{e,me}$ values of the $NaNO_3$ and $(NH_4)_2SO_4$
242 particles at four size deviate from their average values with the maximum of 5.9 % and
243 4.8%, respectively, which are identical with the deviation phenomenon for the $\rho_{e,me}$ of
244 PSL particles. These deviations may be derived from the calibration of particle Dva
245 from the SPAMS. While the R-square of size calibration curve is 0.999, the curve of
246 exponential function is found to slightly deviate from the data points measured by
247 SPAMS. For example, size calibration function has the deviation of -4.4% and 3.1%
248 from the data points of 310 and 740 nm, respectively.

249 Taking the systematic error into account, the slight difference of the $\rho_{e,me}$ values for
250 the four sizes suggests that the ρ_e of $(NH_4)_2SO_4$ and $NaNO_3$ particles is independent of
251 particle size from 250.0 nm to 550.0 nm. It is determined by the definition of effective
252 density used in this study, which keeps constant as long as the χ_a of the particles does
253 not change with particle size for pure compound. The average $\rho_{e,me}$ values of $(NH_4)_2SO_4$
254 and $NaNO_3$ particles are calculated to be 1.7 ± 0.1 and 2.1 ± 0.1 g/cm^3, respectively.

The average $\rho_{e,me}$ values are lower than that the ρ_p of $(NH_4)_2SO_4$ (1.77 g/cm^3) and $NaNO_3$ (2.27 g/cm^3), which is caused that the $\rho_{e,me}$ is determined by both of ρ_p and χ_a. According to Eq. (14), the χ_a of $(NH_4)_2SO_4$ and $NaNO_3$ particles with different D_a are calculated to be 1.04, 1.11, 1.11, and 1.04 and to be 1.03, 1.14, 1.14, and 1.08, respectively. Thus, the average χ_a values of the $(NH_4)_2SO_4$ and $NaNO_3$ particles are determined to be 1.07 ± 0.04 and 1.10 ± 0.05, respectively, which can be used to parameterize their morphology.

The average χ_a values of the $(NH_4)_2SO_4$ and $NaNO_3$ particles indicate that these particles are aspherical. The asphericity of $(NH_4)_2SO_4$ determined by AAC-SPAMS system is consistent with the previous studies reporting that the χ_a of $(NH_4)_2SO_4$ were larger than the value of 1.03 (Zelenyuk et al., 2006; Beranek et al., 2012; Zhang et al., 2016a). However, previous studies found that the $NaNO_3$ particles had different morphology. Zhang et al. (2016a) observed that $NaNO_3$ had the χ_a of 1.09-1.13, indicating its asphericity, while Hoffman et al. (2004) found that $NaNO_3$ particle had a round droplet-like shape even at 15% RH, which was supported by the consistence between the measured value of "anhydrous" droplet density and the calculated value of "anhydrous" solution droplet (Zelenyuk et al., 2005). Eclectically, Tang and Munkelwitz (1994) studied that most of the $NaNO_3$ particles crystallized between 20% and 30% RH but some persisted down to 10% RH to form solution droplets. Notably, the spherical $NaNO_3$ particles at low RH observed by Hoffman et al. (2004) were dried in the sticky carbon tape which might affect the phase transition of droplet-like $NaNO_3$ particles. In this study, most $NaNO_3$ particles were crystallized because the RH of the

aerosol flow carrying the $NaNO_3$ particles was reduced to below 20% through the diffusion drying tube. Besides, the result that the crystallized $NaNO_3$ particles are aspherical is supported by their FWHM values of the D_{va} distributions which are consistent with that of aspherical $(NH_4)_2SO_4$ but wider than spherical PSL (Figures S1 and S2).

3.3 Application of the AAC-SPAMS system for measuring the chemically-resolved D_{ve} and ρ_e

SPAMS can obtain information on the chemical composition of individual particles, implying that the AAC-SPAMS system has the ability to simultaneously characterize D_{ve}, ρ_e and the chemical compositions of particles in real time. It is worth noting that the particles with the largest χ in the actual atmosphere should be freshly emitted soot, which χ is 2.5 (Peng et al., 2016). This largest χ fitly meets the upper limit for the approximation between the χ_t and χ_v (DeCarlo et al., 2004). Therefore, the AAC-SPAMS system can obtain the chemically-resolved D_{ve} and ρ_e values for unknown aerosol particles in the field observation.

As an example, we applied the AAC-SPAMS system to illustrate how the measured D_a, D_{va}, and chemical composition of an individual particle can be used to calculate the D_{ve} and ρ_e for unknown particles. The sampled ~100,000 particles are classified into eight major particle types with distinct chemical patterns of K-rich, EC-S, K-Na, Amine, EC-N-S, OC-N-S and OC-EC-N-S and Metal-rich, representing 97% of the detected particle population. Details of the chemical composition and number fraction of the

299 eight types of particles are presented in the Figures S3 and S4, respectively, which are
300 discussed in the Supporting Information.

301 We used Gaussian fitting to obtain the D_{va} peaks for each particle type with D_a values
302 of 250.0 nm, 350.0 nm, 450.0 nm, and 550.0 nm. Then, we calculated the D_{ve} values of
303 the atmospheric particles with Eq. (11). Table 1 presents the average D_{ve} values of the
304 eight particle types, for which the standard deviation is calculated based on nine
305 samples. The average D_{ve} at D_a values of 250.0 nm, 350.0 nm, 450.0 nm, and 550.0 nm
306 has the following wide ranges: from 188.5 nm to 200.8 nm, 271.9 nm to 295.7 nm,
307 342.5 nm to 428.9 nm, and 397.3 nm to 570.9 nm, respectively, which are caused by
308 the chemical composition differences. The result indicates that particles with
309 significantly different D_{ve} might possess the same D_a. Furthermore, the large standard
310 deviation of D_{ve}, such as 21.9 nm for K-Na at 250.0 nm, 32.3 nm for OC-EC-N-S at
311 350.0 nm, and 44.3 nm for OC-N-S at 450.0 nm, indicates that the D_{ve} of particles is
312 remarkably different even for particles with the same type and same D_a.

313 According to D_{ve} and D_{va}, we calculated the ρ_e of each particle type with Eq. (12).
314 Figure 4 shows the variations of the ρ_e with D_{ve} for nine particle samples. For pure
315 compounds, such as $(NH_4)_2SO_4$ and $NaNO_3$ particle, ρ_e theoretically does not change
316 with particle size. However, the sampled particles have experienced complex
317 atmospheric processes. Therefore, ρ_e has a very wide distribution for each type of
318 particle with a similar D_{ve}. Specifically, the ρ_e of K-Na increases with D_{ve}, while the ρ_e
319 of OC-N-S and OC-EC-N-S decreases with D_{ve}, which may be influenced by the
320 particle shape or the material density. Additionally, the average ρ_e of each type of

particle is in the order from small to large: 1.2 ± 0.2 g/cm^3 for OC-EC-N-S, 1.3 ± 0.2 g/cm^3 for OC-N-S, 1.4 ± 0.1 g/cm^3 for K-rich, 1.4 ± 0.1 g/cm^3 for Amine, 1.5 ± 0.1 g/cm^3 for EC-N-S, 1.5 ± 0.1 g/cm^3 for EC-S, 1.6 ± 0.1 g/cm^3 for K-Na and 1.6 ± 0.1 g/cm^3 for Metal-rich. It is reasonable to find that the average ρ_e of internally mixed particles distributes in the range of their material densities (ρ_m). For instance, mainly comprised of internally mixed sulfate and organics, the OC-EC-N-S, OC-N-S, K-rich, and Amine particles have the average ρ_e between that of sulfate with ρ_m of 1.77 g/cm^3 and organic aerosols with ρ_m of 1.2 g/cm^3 (Cross et al., 2007).

4. Conclusion

We first develop an AAC-SPAMS system to achieve the measurement of the D_{ve} and ρ_e of the particles through characterizing their D_a and D_{va}. The reliability of the AAC-SPAMS system is verified by accurately measuring the D_{ve} and ρ_e of PSL. Applying the AAC-SPAMS system to determine the D_{ve} and ρ_e of $(NH_4)_2SO_4$ and $NaNO_3$ particles shows that these particles are aspherical and their ρ_e are independent of particle size. Coupled with the ability of SPAMS to characterize the chemical composition of individual particles, we conducted a sample proof of the AAC-SPAMS equipment to first simultaneously characterize the D_{ve}, ρ_e and chemical compositions of atmospheric particles, showing the potential application of this system in field observations. The approach achieves the measurement of chemically-resolved D_{ve} and ρ_e, and provides the possibility to determine their quantitative relationship with other particle properties, which would be benefit for further reduction of the uncertainty associated with the

effects of particles on air quality, human health and radiative forcing.

Data availability. Data in this study is available at https://github.com/longer1217/All-figures-data.

Author contributions. The idea for the study was conceived by LP and GHZ. All experiments were performed by LP with the assistance of LL. LP wrote the paper which was reviewed by GHZ and XHB. All co-authors discussed the results and commented on the manuscript.

Competing interests. The authors declare they have no conflict of interest.

Acknowledgment

This work was supported by the National Nature Science Foundation of China (41775124 and 41877307), Natural Science Foundation of Guangdong Province (2019B151502022), and the Guangdong Foundation for the Program of Science and Technology Research (2019B121205006 and 2017B030314057). The authors also gratefully acknowledge Cambustion Ltd., UK for providing the AAC and Hexin Analytical Instrument Co., Ltd., China for providing the SPAMS.

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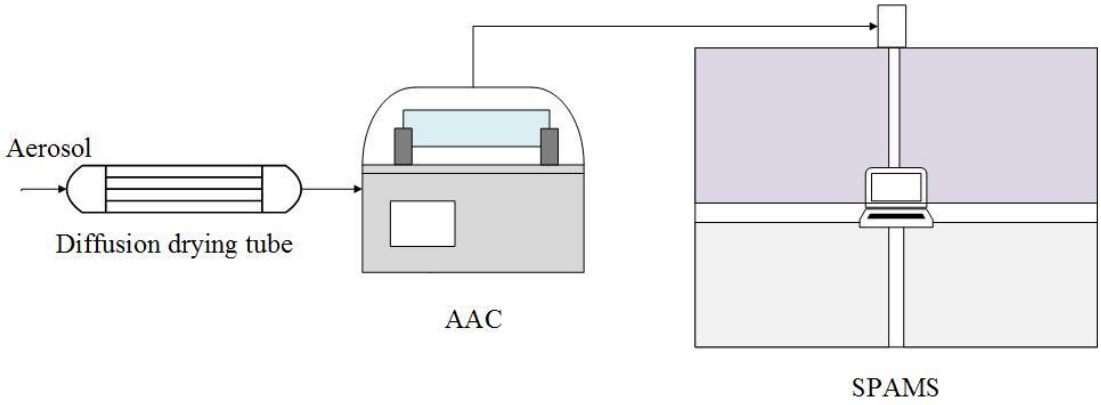
Table 1. The measured mean D_{ve} and its standard deviation for the eight particle types at D_a values of 250.0 nm, 350.0 nm, 450.0 nm, and 550.0 nm from nine round measurement.

D_a (nm)	K-rich	EC-S	K-Na	Amine
250.0	193.1 ± 8.2	192.2 ± 8.1	193.8 ± 21.9	190.6 ± 4.6
350.0	284.0 ± 28.4	280.8 ± 9.3	271.9 ± 18.0	284.8 ± 18.2
450.0	364.7 ± 21.1	357.8 ± 6.9	342.5 ± 7.3	367.9 ± 9.7
550.0	416.6 ± 28.3	439.5 ± 5.4	397.3 ± 29.7	442.5 ± 7.4
D_a (nm)	**EC-N-S**	**OC-N-S**	**OC-EC-N-S**	**Metal-rich**
250.0	188.5 ± 5.9	200.8 ± 17.9	195.4 ± 8.9	189.0 ± 6.7
350.0	281.3 ± 9.3	295.7 ± 29.8	294.0 ± 32.3	277.0 ± 9.1
450.0	358.0 ± 5.8	398.3 ± 44.3	428.9 ± 24.0	342.9 ± 10.0
550.0	453.2 ± 16.4	547.4 ± 14.7	570.9	407.4 ± 14.5



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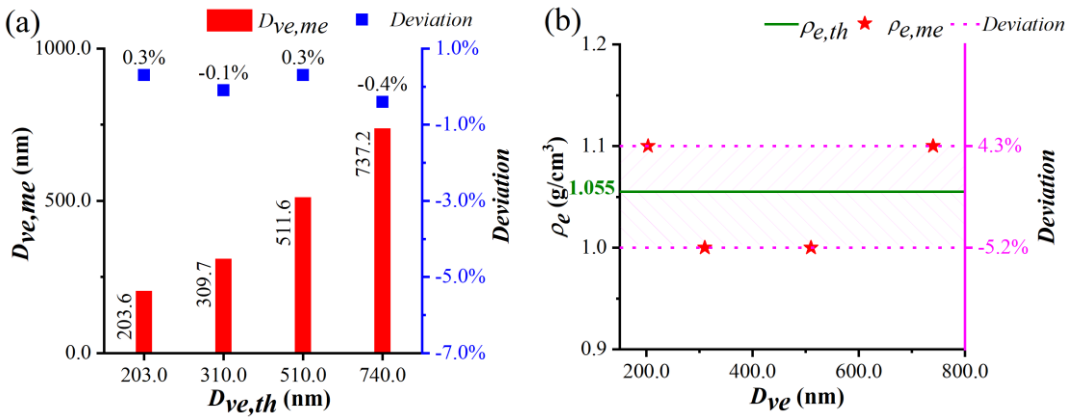
504 **Figure 1.** Schematic diagram of the AAC-SPAMS system (0.3 lpm). The diffusion drying tube is

505 filled with orange silica gel, which reduces the RH to 5-15%.



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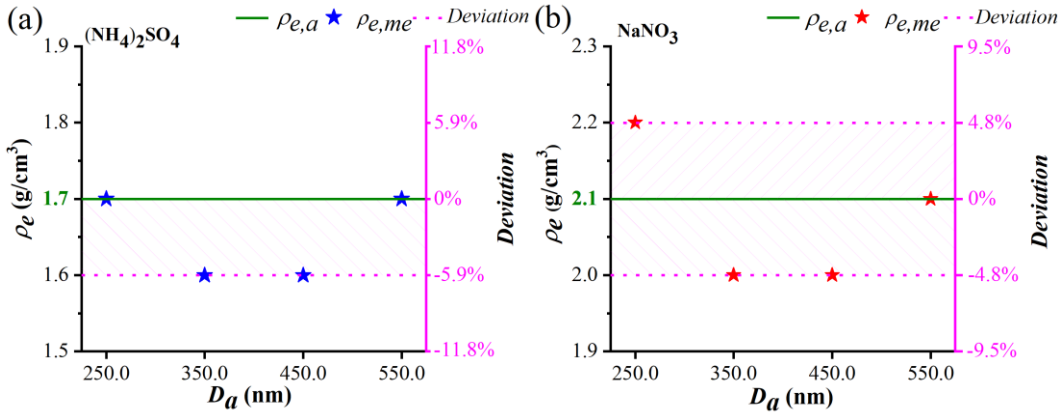
508 **Figure 2.** (a) Comparison between the measured D_{ve} ($D_{ve,me}$) and the theoretical D_{ve} ($D_{ve,th}$) of the

509 PSL particles. (b) Comparison between the measured ρ_e ($\rho_{e,me}$) and the theoretical ρ_e ($\rho_{e,th}$) of the

510 PSL particles.



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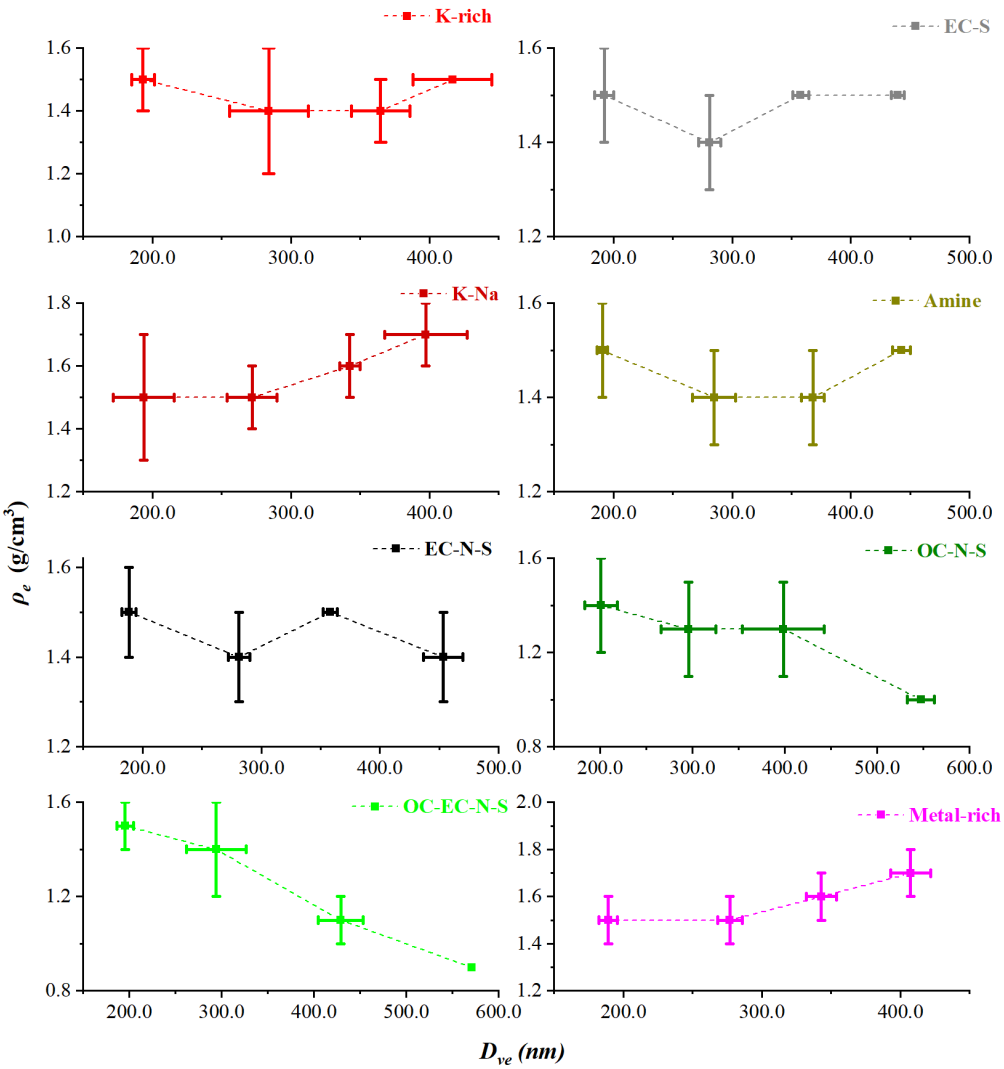
513 **Figure 3.** (a) Comparison between the measured ρ_e ($\rho_{e,me}$) and average ρ_e ($\rho_{e,a}$) values of the

514 $(NH_4)_2SO_4$ particles. (b) Comparison between the measured ρ_e ($\rho_{e,me}$) and average ρ_e ($\rho_{e,a}$) values of

515 the $NaNO_3$ particles.



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518 **Figure 4.** Variation in ρ_e of the eight particle types with D_{ve}. The solid lines represent the rang of

519 the ρ_e and D_{ve} measured from nine rounds, and the data points stand for the average values.