Interactive comment on "Tandem configuration of differential mobility and centrifugal particle mass analyzers for investigating aerosol hygroscopic properties" by Sergey S. Vlasenko et al.

We would like to thank Referee #3 for the constructive criticism and suggestions for improvement that were taken into account upon manuscript revision. Responses to individual comments are given below.

Major Comments (#1):

1. Since the paper is describing a relatively new methodology, greater detail is required to explain the advantages and drawbacks of the proposed system, including:
a. A discussion on the effects of multiply-charged particles, system resolution and the effect of the experimental design parameters. For example was the intention of introducing the 1 lpm of humidified air prior to the CPMA inlet to decrease the residence time of the aerosol in the CPMA and thus reduce heating effects? The reduction in CPMA classifier resolution due to this increased flowrate should be mentioned.
b. The resolution the CPMA was operated at and how it compares to the width of the unclassified particle size distributions measured. It would be beneficial to explain that operating at higher resolutions, requires higher rotational speeds and thus additional heating effects.
c. A discussion of possible data inversion techniques that could be applied to the mass-to-charge distribution measured by the CPMA and the method that was chosen for this work. For example, asymmetric normal distribution or a lognormal distribution (Tajima et al. 2011; Johnson et al. 2013) or convolution of the DMA and CPMA transfer functions (Emery 2005; Barone et al. 2011).
d. A discussion on the system uncertainty and its propagation into the final results, incorporating DMA and CPMA setpoint uncertainty.

Response

We agree with referee and tried to improve the text. The air flow system was designed to provide required RH and residence time that determined the flowrate. The resolution was selected for the given flow rate to decrease heating.

Change in manuscript

The following fragments are added to manuscript in response to comments (a-d)

"Thus, a CPMA selects particles with a mass (m^*), provided that the charge on the particles is the same and known (Olfert et al., 2006)

$$m^* = \frac{zeV}{\omega_c^2 r_c^c \ln(r_2/r_1)}, \quad (1)$$

where V is the voltage between inner and outer cylinders with radii r_1 and r_2, z is the number of elementary charges e on the particles, $r_c = (r_1 + r_2)/2$ – centre radius, and ω is angular velocity at r_c. To improve the transfer function of the classifier, the outer electrode rotates slightly faster than the inner one, producing a stable system of forces (Olfert and Collings, 2005). The particle mass analyzer was operated in the step-by-step scanning mode, where rotation speed and applied voltage are varied in a discrete way to scan the desirable particle mass range. The CMPA, in conjunction with the condensation particle counter (CPC) (TSI model 3787), measured the particle mass based spectrum as a function of the applied RH history. At each step in the scanning mode the detector (CPC) registers the total particle concentration ΔN passed through the CPMA . This concentration mainly depends on the width and the amplitude of the CPMA transfer function which is essentially triangular in case of neutral stability. The mass setpoint defined by (1) correspond to the centre of the transfer function. The width Δm of the function at the half-maximum level determines the mass resolution of the CPMA. In scanning mode the resolution parameter of the CPMA, $R=m^*/\Delta m$ is automatically maintained at the preset value. Therefore, the CPMA provides the averaged mass

spectral density - $\Delta N/\Delta m$ or in logarithmic scale $\Delta N/\Delta \log(m) = \Delta N/\log(1+1/R_m)$. The resolution parameter of the CPMA depends on voltage, rotational rate, air flow and indirectly upon desirable mass range. Its selection is a compromise between the contradictory conditions. For example the high resolution requires rapid electrodes rotation and heightened voltage that increased heat producing and risk of discharge inside the CPMA. In the present work we used by default R = 5, that corresponds to geometric standard deviation 1.08 and 1.03 in the mass and size scales respectively".

"Obviously the concept of the described method is quite identical to widely used HTDMA technique. This approach deals only with modal values of relatively narrow distributions, that makes it less sensitive to the effects of such instrumental factors as transport losses, detection efficiency and multiple charging . Following Rawat et al. (2016) and Stolzenberg & McMurry (2008) the measured particles concentration can be linked to mass-based distribution function *dn/dm* through the equation :

$$\Delta N(m_i) = \sum_{z=1}^{\infty} \int_0^{\infty} \varepsilon(m)\Theta(z,m,m_i) f(z,m) \frac{dn}{dm} dm \quad , \qquad (3)$$

where i is a number of the step in the CPMA scanning mode, m_i and Θ are the mass setpoint and the respective transfer function, $f(z,m)$ is the fraction of particles of mass m with z elementary charges, $\varepsilon(m)$ is transport efficiency through system tubing. In most of our experiments the particles distribution was rather narrow with mass geometric standard deviation of about 1.10 which is slightly more than mass geometric standard deviation of the CPMA transfer function. Firstly it means a clear resolution of peaks of multiple-charged particles (Symonds et al., 2011; McMurry et al., 2002). For particles passed through the DMA with mobility diameter setpoint D_b=70 nm the registered by the CPMA the double to single charged particles mass ratio is about 1.7 that is considerably large than the width of the particles distribution as well as the CPMA transfer function. Secondly the variations in $\varepsilon(m)$ and $f(z,m)$ across the width of distribution function are relatively small that means negligible shift in position of maximums of $\Delta N/\Delta m$ and *dn/dm* though their amplitude values and widths are different.

The Twomey-Markowski algorithm (Markowski 1987; Alofs & Balakumar 1982) was applied to inverse the equation (3) and estimate the mass-based distribution function as described in detail in supplemental information to Rawat et al. (2016). We used provided there equations for transport and detection efficiency converted in the mass scale. For deconvolution we employed the idealized triangular transfer function recommended by the manufacturer and measured by Olfert et al. (2006). The results are shown in Fig.2 (dash curves). The deconvoluted functions are narrower than experimental distributions but the modal mass values of $\Delta N/\Delta m$ and *dn/dm* agree within 2%. This inversion procedure was applied to the CPMA measurements though we consider it is not critical in this study. Some exceptions are discussed below.

The precision of the CPMA particle mass measurements mainly depends on the uncertainties of voltage , rotation speed, air flow rate and profile between electrodes. The voltage and speed are software controlled inside the CPMA within 0.02% and registered in data output files. Calculated from this data (using Eq.(1)) the mass setpoint uncertainty was less than 0.1%. The air flow rate seems the most unstable factor which fluctuated within 2-3 %. The flow rate affects the CPMA resolution and not the mass setpoint, so its contribution to the mass uncertainty is difficult to account. Practically the mass uncertainty determined as standard deviation of repeated measurements that took into account the DMA setpoint uncertainty as well. There were a lot of dry aerosol measurements distributed throughout the experimental period and for dry aerosol the mass uncertainty was 5% that agree with the results of other researches (McMurry et al., 2002; Joynson et al., 2015). The number of repeated measurements at a

certain RH is not so large and though the measured mass usually were scattered within 5% we assumed the mass uncertainty in humid conditions equal to the transfer function width (8%). According to Eq.(2b) this uncertainties translates into a 10% uncertainty in G_m"

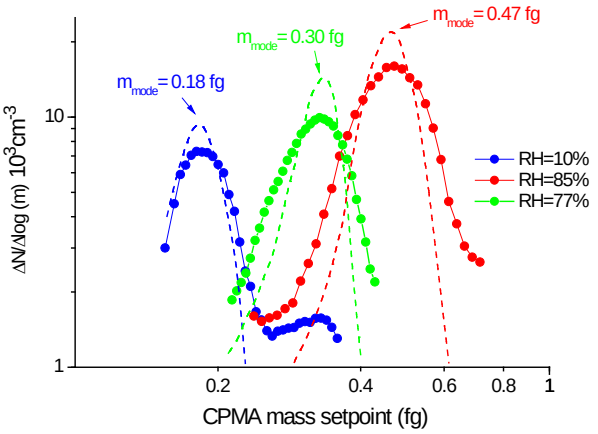

Figure 2. HCPMA measured particle number mass distribution of ammonium sulfate at different RH with initial dry particle modal mass m_d = 0.18 fg. The indicated mode is the modal value of the particle mass distribution used for the mass growth factor (G_m) calculation. Symbols and solid lines – experimental averaged mass spectral density ΔN/Δlog (m). Dashed lines - mass-based distribution function after application of inversion procedure to primary data.

Comment from Referee (#2)

2. The discussion on contact efflorescence on Page 6 assumes that even though the particle contacts a charged surface indirectly through the surface crystals the particle's charge does not transfer and that the CPMA centrifugal force is sufficient to separate the particle from the surface crystals after efflorescence transition. Was there evidence of crystal formation on the CPMA inner electrode during classifier cleaning? Furthermore, if the inner electrode surface crystals grew large enough to alter the CPMA classifier's gap, arcing between the cylinders (especially at higher RHs) would likely become an issue first.

Response

Contact efflorescence is considered as possible reason for the observed bimodal distributions. This is only a hypothesis without any reliable evidence. We agree that charge transfer may happen when particle contacts the electrode or the previously precipitated particle, but the final result of it is uncertain. When cleaning we saw a slight white sediment on the both cylinders (like DMA) but it does not prove anything. The cleaning procedure was regular enough to prevent arcing.

Change in manuscript

The following clarifying sentence has been added:

"It should be noted that contact efflorescence inside CPMA was suggested as the most plausible explanation for the observed early ERH. Additional experimental and modelling studies are needed to test this hypothesis".

To avoid misunderstandings, in conclusion the following text has been removed:

"We suggest that under controlled composition of particles on the electrode surface, the HCPMA system could be additionally used to study isochemical and heterochemical contact efflorescence".

Minor Corrections (#3):

1. Given the CPMA measures a mass-to-charge distribution and the variety of data inversion techniques, each mention of particle mass should be further clarified, such

as changing "mass" on Page 1 Line 16 to "modal mass".

R**esponse**

To improve the terminology we introduced where appropriate in text the following terms "the averaged mass spectral density","the mass setpoint", " the center of the transfer function" ," modal mass". Besides we applied inversion procedure to our data.

Comment from Referee (#4)

2. On Page 2 Line 16, it should be reflected that the DMA-HCPMA configuration has been utilized by others to measure the mass-based hygroscopicity of nanoparticles, such as Johnson et al. 2015.

R**esponse**

Johnson et al. (2015) paid main attention to particles effective density changing due to water uptake. This paper is referenced on page 3, line 3. We believe it would be better to add some words here.

Change in manuscript

In the last work the combination of DMA and CDMA was used to measure mass growth factor of tobacco smoke particles as function of increasing RH. This technique is more similar to ours.

Comment from Referee (#5)

3. Referring to Page 14 Line 20, did the temperature of the CPMA stabilize after extended periods of continuous operation? If so, at what temperature? This information would be valuable for others applying this method in the future.

R**esponse**

After a prolonged continuous operation (3-4 hours) the temperature of the CPMA usually stabilizes at 4-6 degrees above room level depending on average rotation speed. The stable CPMA temperature means the constant temperature of water bath.

Change in manuscript

Usually the CPMA temperature stabilized at 4-6 degree above room level after 3-4 hours of continuous operation depending on average rotation speed.

Comment from Referee (#6)

4. On Page 3 Line 23, it would be valuable to mention that similar to the DMA, the upper
RH limit of the CPMA is limited by voltage arcing between the classifier cylinders.

R**esponse**

The voltage between cylinders depends on desirable mass/size range and resolution. The higher voltage is required to classify more massive particles with the same resolution. In most of our experiments the voltage did not exceed 200 V that corresponds electric field 2kV/cm. This field is at least twice less than in DMA, so there was no arcing even at 98% RH. It may be potential advantage of the method. But the high RH is difficult to control and the intensive water condensing in cooler tubes after the CPMA prevents flow stability and proper operation of the CPC. That was the reason of the upper RH limit in our work.