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 Peter McMurry for the constructive criticism and suggestions for improvement that were taken into account upon manuscript revision. Responses to individual comments are given below.

Major concerns:
Comment from Referee (#1).

(1) My major concern is the cavalier discussion of measurement technique fundamentals. Figure 2 shows particle number mass distributions with no explanation as to how they were obtained. In fact, given the relatively broad transfer function of instruments such as the CPMA, obtaining number mass distributions is not straightforward. The literature includes some pertinent information, which is not discussed. Park et al. (Park et al. 2003) reported on measurements of aerosol mass distributions as a function of mobility diameter from DMA-APM measurements. Their method assumed that particles classified by the DMA had only a single mass (the "modal mass" in the language of the paper under review), which is only approximately true even for chemically homogeneous aerosols. Because the transfer function of a DMA is triangular, mobility-classified particles have a distribution of masses and that distribution affects APM (or CPMA) data. The transfer function of the APM (or CPMA) is even broader than that of the DMA, so at the voltage corresponding to the "modal mass" some particles of every size leaving the DMA penetrate through the APM (or CPMA). Furthermore, ambient aerosols of a given mobility size may include particles of that are chemically and morphologically distinct, which leads to multimodal mass distributions. These subtleties need to be acknowledged in a measurement techniques paper. More recently, Rawat and coworkers (Rawat et al. 2016) developed an inversion algorithm for obtaining two dimensional number distributions (as a function of mobility diameter and mass) from DMA-APM measurements. Equation 2 of that paper shows the relationship between measured number concentrations downstream of the APM, and operating characteristics of the DMA-APM apparatus (flow rates, voltages, etc., which determine the DMA & APM transfer functions.) Extending their approach to DMA CPMA data should be possible provided the CPMA transfer function is sufficiently well known. However, Vlasenko and coworkers do not discuss this conceptually important background. I suspect the number mass distributions shown in Figures 2 & 4 were obtained by assuming that the number mass distribution was constant at a given CPMA classifying voltage. Given the narrowness of the sampled aerosol distribution and the breadth of the CPMA transfer function, that is a not a good assumption. Most previous DMA-APM (or CPMA) work has involved working with raw data: i.e measurements of number concentration downstream of the CPMA as a function of CPMA classifying voltage (or equivalently, modal mass), and this is a valid approach. If the authors choose not to use a mathematically justified approach for inverting data to obtain number distributions with respect to mass, I would recommend that they stick to analysis of the raw data. This would involve revising figures 2 & 4 to show only N versus V_{CPMA}, or equivalently, N versus modal mass. The figures 3 & 6 are based on the modal mass (i.e., the value that corresponds to the peak value in the $N(V_{CPMA})$ measurements), so as far as I can tell the distribution functions are not required for the analyses that were done.

Response
We acknowledge that some questions need more detailed explanation and some additions were inserted in the text. But we believe that the CPMA transfer function is narrower than the DMA transfer function (geom. st. dev. 1.03 against 1.05 in size scale) which determines the width of

input particles distribution. Besides we applied inversion procedure to our data as recommended by the all referees.

50 **Change in manuscript**

The following fragments are added to manuscript in response to comments:

"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)

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

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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).

60 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

65 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

70 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

75 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

80 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 registered particles concentration can be linked to mass-based distribution function dn/dm through the equation :

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

85 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

90 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 larger 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 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.
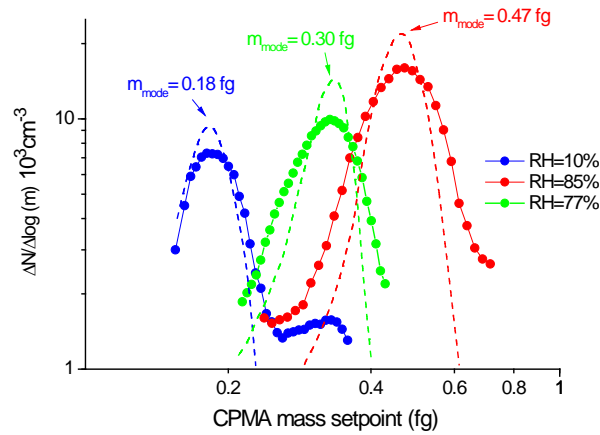

Figure 2. HCPMA measured particle number mass distribution of ammonium sulfate at different RH with initial dry particle modal mass $m_d = 0.18$ fg. The indicated mode is the modal value of the particle mass distribution used for the mass growth factor (G_m) calculation. Symbols and solid lines – experimental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

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"

Comment from Referee (#2)

(2) While I this methodology is conceptually appealing, I do not believe the paper delivers on the abstract's promise: "The direct measurements of humidified particle mass allow avoiding complications that occur in the commonly used mobility-diameter-based HTDMA technique due to poorly defined particle morphology and density." It is clear from results of the paper that heating within the CPMA and the broad transfer function of the CPMA lead to complications that are at least as great as those that occur with the HTDMA. The abstract fails to provide a straightforward assessment of the proposed measurement technique's weaknesses. The abstract needs to be forthright about identifying those weaknesses.

Response

We believe that heating is not a crucial complication and its effect can be compensate by different means. Perhaps our way is not optimal, but it provides satisfactory results. The breadth of the CPMA transfer function depends on operational parameters and can vary within certain range. In some operation modes it is narrower than the DMA transfer function. So we believe it is not an inherent weakness of the technique to note it in the abstract. We added some phrases relating to that in main text.

Change in manuscript

"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 the default R = 5, that corresponds to geometric standard deviation 1.08 and 1.03 in the mass and size domains respectively."

Minor Concerns:

Comment from Referee (#3)

(1) Based on results presented in the paper, I think a strong case can be made that the HTDMA method is in principle better for measuring deliquescence and efflorescence thresholds. It is easier to operate a HTDMA under isothermal conditions.

Response

We agree that currently DRH and ERH measuring with the CPMA is worse than those obtained by HTDMA method due to the relatively large RH uncertainty. We are working on this issue.

Comment from Referee (#4)

(2) On p. 5 it is stated"... for AS and NaCl particles with initial mobility diameter Db=60 nm and dry masses of 0.18±0.01fg and 0.21±0.01fg."I assume"±0.01"corresponds to the estimated uncertainty in the modal mass. While the modal mass may be known with high certainty, the relatively broad transfer function of the CPMA ensures that the range of masses exiting the CPMA greatly exceed this value. The authors need to explain why the modal mass is the proper variable even though sampled mass distributions might have been multimodal (see point 3 below).

Response

We have developed the technique assuming narrow unimodal input distribution. In this case the modal mass is a reasonable parameter to describe the hygroscopic growth and it can be determined within 5%. The cases where particles distributions proved to be broad or even multimodal need more careful consideration. Of course the positions of peaks are determined with more uncertainty. We tried to explain that in those cases where the results are not very reliable.

Comment from Referee (#5)

(3) The abscissas of Figures 2 & 4 are labeled "Particle Mass". I recommend they be relabelled "Modal Mass". The reader needs to understand that, in fact, particles covering a broad range of masses were present at each CPMA voltage. The importance of this is emphasized by the discussion on p. 6 "..the output aerosol in dehydration mode is a mixture of droplets and dry particles.." If the CPMA transfer function were sufficiently narrow, it would have been possible to distinguish between droplets and dry particles. It is also possible (but not guaranteed) that his could have been achieved if an inversion method similar to that discussed by Rawat et al. had been used to retrieve the true mass distribution. In any event, this phrase supports my argument that these plots do not show mass distributions and need to be replotted.

Response

Following this recommendation we applied inversion procedure to our data and corrected the terminology. Changes in the text have described above.

The abscissas of Fig.2 and Fig.4 were relabelled as "CPMA mass setpoint (fg)" .

Comment from Referee (#6)

(4) I am confused by Figure 3. For AS, the blue "+" is labelled "non-prompt efflorescence "while for NaCl ,the blue"+"is labeled "Non-prompt deliquescence". The text on p. 5 states "For both AS and NaCl particles, intermediate growth factors between dry and deliquesced particles were observed (Fig. 3 - blue crosses)." The text contradicts the figure label.

Response

That is a sad mistake. Fig. label is corrected.

Comment from Referee (#7)

(5) I am not convinced that contact efflorescence explains the results and that this might be an approach for studying contact efflorescence (see Figure 5 and discussion on p. 6). Wouldn't it be possible to test this idea by carrying out measurements extending from high voltages, where all particles reach the inner rotating electrode, to low voltages, where all particles reach the outer rotating electrode? The proportion of particles undergoing contact efflorescence should be higher at the low or high voltages, right? Is there any evidence for this?

Response

Contact efflorescence is considered as a possible reason for the observed bimodal distributions. This is only a hypothesis. To confirm or disprove this assumption one needs to fulfill a special study that beyond the issue of the paper. A proposal to vary voltage seems promising but difficult to implement because voltage related to rotation speed, mass resolution and so on. We believe that trajectories of particles need to be simulated inside the CPMA taking into account the possibility of contact efflorescence.

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".

Comment from Referee (#8)

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(6) Does the extent of non-prompt efflorescence and deliquescence change if measurements are carried out when the CPMA is first turned on (i.e., before frictional heating has had time to warm it up)?

Response

225 There were a few measurements of efflorescence and deliquescence at the beginning of operation. We rewieved our data from this point of view but failed to reveal any dependence on the temperature inside the CPMA.

Comment from Referee (#9)

230 In summary, the proposed measurement methodology offers clear conceptual benefits over other methods such as the HTDMA for studying particle phase transitions and hygroscopicity. However, the measurements that are reported reveal limitations on measurement accuracy that may difficult to overcome. Furthermore, I question the validity of Figures 2&4. Because the method, in principle, adds to what can be learned from other techniques, I feel it would merit 235 publication after the authors respond to the points raised above.

Park, K., D. B. Kittelson and P. H. McMurry (2003). "A closure study of aerosol mass concentration measurements: comparison of values obtained with filters and by direct measurements of mass distributions." Atmospheric Environment 37(9-10): 1223-1230. Rawat, V. K., D. Buckley, S. Kimoto, M.-H. Lee, N. Fukushima and C. J. Hogan Jr. (2016). "Two-240 dimensionalsize-massdistributionfunctioninversionfromdifferentialmobilityanalyzer-aerosolparticlemassanalyzer(DMA-APM)measurements."Jounrnalof Aerosol Sci. 92: 70-82. Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-249, 2016.

Response

All concerns have been accounted for and additional literature was examined and included in the 245 reference list.