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 #2 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 from Referee (#1)

A more thorough study into the uncertainties of measurement would be ideal, perhaps even as an appendix or SI. Though not common (arguably it should be), error propagation for measurement data would be very helpful in drawing conclusions as to the benefits or drawbacks of measurement techniques. How accurate is a standard HTDMA, for example? Few papers involving the use of HTDMA quantify the errors, yet draw conclusions regarding cloud formation and aerosol hygroscopicity, which in turn propagate through to κ values and into models. This is not good practice, and it would be useful to at least include some kind of error propagation (e.g. flows, voltages, etc etc) through to final values. The authors state that the difference between experiment and theoretical growth factor values does not exceed 10%. If the uncertainties are above 10% for the system (likely), then this is indeed good agreement. The authors make no mention of the ZSR assumption of volume additivity. This seems like a near-ideal experimental setup to more accurately probe this conventional assumption. Perhaps ideally, dual-CPMA or CPMA-HDMA would be employed as the first DMA is still dependent on shape factor and morphology whereas particle mass is always particle mass. Comment?

Response

It is a fair comment and we tried to pay more attention to errors analysis. But we still believe that the HTDMA errors are beyond the scope of this article. We are planning to combine HTDMA and HCPMA, so the required analysis may be the topic of the future paper.

Change in manuscript

The following text is added.

"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"

Minor comments:

Comment from Referee (#2)

Final sentence of the abstract is muddled. It would read better as: "Direct measurements of particle mass avoid the typical complications associated with the commonly used mobility-diameter based HTDMA technique (mainly due to poorly defined or unknown morphology and density)."

Response

We agree with this observation and make the proposed revisions

Change in manuscript

55 The last sentence of the abstract is replaced by "Direct measurements of particle mass avoid the typical complications associated with the commonly used mobility-diameter based HTDMA technique (mainly due to poorly defined or unknown morphology and density)."

Comment from Referee (#3)

60 *Page 2 Line 6: arguably the aerosol is quasi-monodisperse and not truly monodisperse, due to multiple charging.*

R**esponse**

We agree that truly monodisperse aerosol is a kind of idealization and never found in nature or laboratory. But we believe that words "monodisperse aerosol" are often used approximately for
65 brevity.
Nevertheless some clarification will be added to the text.

Change in manuscript

"The selected particles are not truly monodisperse due to multiple charging effects, non-ideality of DMA transfer function etc. However the width of output size distribution is small enough to
70 consider the aerosol as "quasi-monodisperse.""

Comment from Referee (#4)

Page 2 Line 32: This would be the ideal location to introduce the CPMA in more detail. E.g. "Mass classifiers started with the APM and improved with the CPMA" – the CPMA has a higher
75 *penetration efficiency for any given mass than the APM*

R**esponse**

Perhaps the referee is absolutely right, but we have no practical APM experience and so we are not competent enough to compare the APM and CPMA in detail. We believe that the almost twenty-year history of the CPMA deserves a detailed and thorough review written by researches
80 who have extensive experience with the technique.

Comment from Referee (#5)

Page 3 Line 1: Please check Kondo et al. 2006 for more references; and note that McMurray et al. 2002 conclude the DMA-APM to have around 5% uncertainty (this paper is already
85 *referenced)*

Response

We thank the referee for useful reference.

Change in manuscript

"Kondo et al. (2006) mounted the heater upstream the DMA and used the DMA+APM technique
90 to measure a relationship between mass and size of non-volatile particles in ambient air."

Comment from Referee (#6)

Page 3 Line 4: Novel application

R**esponse**

95 Done

Comment from Referee (#7)

Page 3 Line 19: quasi-monodisperse rather than near-monodisperse

Response

100 The word "near-monodisperse" is used in literature (Geller et al., 2006 in reference list of discussion paper), but we assume that the "quasi-monodisperse" is more appropriate.

Comment from Referee (#8)

Page 4 Line 5: technically, the CPMA classifies particles by their mass: charge ratio, not merely
105 *mass*

R**esponse**

Changed as suggested.

Change in manuscript

"according to their mass to charge ratio"

110

Comment from Referee (#9)

*Page 4 Line 11: the CPMA outer cylinder spins 3% faster ((33/32)-1)*100=3.125 %)*

R**esponse**

That is a sad mistake. The text was corrected.

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Comment from Referee (#10)

Page 4 Line 15: arguably, this is not actually a number-mass distribution. It is a distribution of average masses. No inversion has been performed. This terminology should be thoughtfully considered throughout the manuscript.

120   **Response**

We agree that terminology needs elaboration. To improve the terminology we introduced "the averaged mass spectral density",,"the mass setpoint", " the center of the transfer function". Besides we applied inversion procedure to our data.

Change in manuscript

125   The following text is added:

"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)

130   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

135   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

140   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

145   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

150   geometric standard deviation 1.08 and 1.03 in the mass and size scales respectively".

Comment from Referee (#11)

Page 4 Line 25: "were directly entered" should be "entered"

155   R**esponse**

The text is revised as recommended.

Comment from Referee (#12)

Page 5 Line 13: Though I understand it's common, it's sloppy/confusing to write AS for ammonium sulphate, as that would make sodium chloride SC. (NH4)2SO4 would be correct.

160   R**esponse**

Changed as recommended except Sec.3 where AS used as subscript.

Comment from Referee (#13)

165 *Page 5 Line 26: Not enough emphasis is placed on mass error of 10% translating to size error of 3%. This is where the DMA-HCPMA technique has the potential for significant benefit over some HTDMA measurements, should other issues be addressed.*
Response
We agree that HCPMA has some potential advantages but consider it would better to emphasis
170 after gaining more experience in practical measurements.

Comment from Referee (#14)
Page 6 Line 6: . . . artefact of this technique
Response
175 The text is revised as recommended

Comment from Referee (#15)
Page 6 Line 17: It is important to note that, as with the DMA, any change of the particle water uptake. . .
180 *Response*
The text is revised as recommended

Further comments (#16):
185 *Though it is really the place of the authors to address referee comments, the first Referee is not correct in stating that the "transfer function of the APM or CPMA is even broader than the DMA", and this should be addressed. The transfer function of an instrument is the relationship between its input and its output. For the CPMA, it relates the mass setpoint to the ratio between the concentration of aerosol downstream and upstream of the CPMA. The resolution of the*
190 *CPMA is set by the width of the transfer function, and the maximum penetration by its height. For the case of neutral stability the transfer function of the CPMA is essentially triangular, and theoretically extends to 100% transmission at its peak (Figure 1):*
It is of course possible to pre-classify with a DMA, but the highest resolution of the CPMA in size terms is much higher than any available DMA. However, broadening as with HTDMA
195 *instruments is non-trivial and should be discussed. I agree that the inversion developed by Rawat et al. (2016) should at least be discussed in this paper. Regarding point (3) raised by Referee 1; the CPMA transfer function is not broad in mass-space. I agree that a broad range of masses enter the CPMA from the DMA, as the DMA's output will cover a range of masses as it's a mobility classifier. I refer the authors to my earlier comment regarding "average particle mass",*
200 *though "modal mass" is probably more accurate as stated by Referee 1. For proper mass distributions the inversion by Rawat et al., or similar, should be used.*
Response
We agree with all referees that inversion procedure should be applied to the CPMA data to obtain mass distribution function. But we believe it is not critically needed in our approach
205 because it based on modal mass measurements. Exception – dehydration hysteresis. We decided to employ the inversion algorithm to our data to remove objections.
**Change in manuscript**
The following text is added:
"Obviously the concept of the described method is quit identical to widely used HTDMA
210 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 registered particles concentration can be linked to mass-based distribution function *dn/dm* through the equation :

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

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*

220   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

225   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

230   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

235   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."

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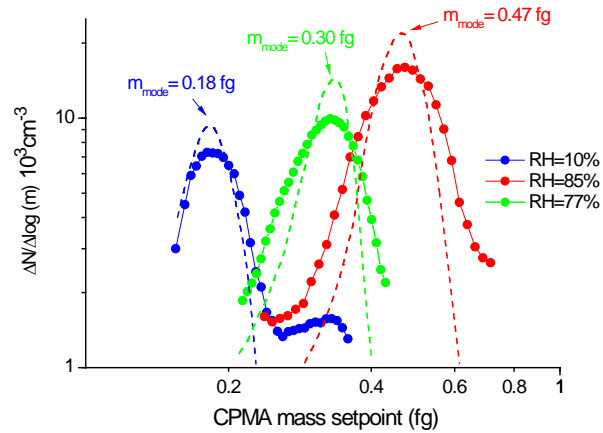
Figure 2. HCPMA measured particle number mass distribution of ammonium sulfate at different RH with initial dry particle modal mass m_d = 0.18 fg. The indicated mode is the modal value of the particle mass distribution used for the mass growth factor (G_m) calculation. Symbols and solid lines – experimental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