

Interactive comment on “A new experimental approach to study the hygroscopic and the optical properties of aerosols: application to ammonium sulfate particles” by C. Denjean et al.

Anonymous Referee #2

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The paper presents an experimental setup to measure hygroscopic and optical properties using a newly constructed chamber, a humidified TDMA and other instruments. Although the experimental setup will likely lead to very useful future research results, I must recommend that the manuscript be rejected in its present form. Based on the results shown and my interpretation of the technical description of the various instrument systems, it appears that one of the major conclusions, that dry ammonium sulfate uptakes water at relative humidities below the deliquescence point, is based on one or more measurement artifacts. I recommend that additional tests be performed on the humidified SMPS to verify that when it is operated at RHs below 80% that the sampled

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particles from the chamber have not actually already deliquesced so that the SMPS measurement is in fact being performed on the efflorescence branch, or that some other measurement artifact (for example hysteresis from water uptake in hydrophilic filters) is causing the observed growth below deliquescence.

The authors claim that their results of water uptake growth by ammonium sulfate aerosol below 30% RH in the humidified SMPS but not the HTDMA is evidence that previous HTDMA studies did not expose the sampled aerosol to elevated RH for long enough times. I believe this claim is mistaken. The deliquescence property of ammonium sulfate (and other common aerosol salts) is a fundamental physico-chemical property of the salt, the HTDMA results that demonstrate the deliquescence point actually support the proper operation of the HTDMA technique. If the residence time were too short, then the historically measured HTDMA growth factors would likely also not agree with theory, however, measured particle growth with elevated RH (even at RH's below the deliquescence point after deliquesced particles are dried) do routinely agree with theory within a few percent for well functioning systems.

I am guessing that what is happening with the strange water uptake observations below the deliquescence point of ammonium sulfate is either unexpected deliquescence of the particles inside the chamber or sample line leading to the SMPS or some kind of hysteresis of water vapor release from hydrophilic filters in the humidification system leading to RH gradients and particle growth. The description of the experimental setup is not detailed enough to allow me to know for certain that this is the case.

The time dependent transient growth models of water uptake by sub micron salts indicate that the relevant timescales to reach equilibrium are on the order of milliseconds for very small (10's of nanometers) to tenths of seconds (several 100 nanometer) diameter particles. The model results are not consistent with the statement that residence times in typical HTDMA humidifiers are too short.

Without deeper supporting evidence, I would attribute the observations that growth by

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ammonium sulfate occurred at RHs as low as 30% to a problem with the experimental setup where the atomized ammonium sulfate droplets were not dried to RHs below the efflorescence RH (about 40%) or were exposed unknowingly to elevated RH so they were not in size-equilibrium with the RH measured in the chamber and/or the sheath humidification system when size selected by the SMPS.

I recommend that the authors carefully review their experimental setup and perform additional tests of the above possible issue.

With respect to the HTDMA technical description it is not clear that there is a RH and temperature sensor on the sheath flow of the upstream DMA. If there is not, there should be.

I would also caution the authors that thin film capacitive RH sensors will shift response when exposed to VOCs, please be sure to check the calibration after any exposures to VOCs during experiments.

Other questions:

in the abstract the claim is made that the complex refractive index can be obtained - but it appears only the real component of the refractive index can be derived from the technique, or at least in this paper, since only ammonium sulfate was studied. For this paper since no absorbing species are studied, 'complex' should be replaced with 'real' when discussing the refractive index.

A If this is true the technique does not retrieve the complex refractive index but the real component of the refractive index.

page 6937 line 18-27: reference is made to previous studies running an OPC behind a DMA to determine refractive index. I believe the work by Sorooshian et al. Aerosol Science & Technology, 42, 445-464, in addition to work by Stolzenburg, and Covert (also AS&T) pre-date the referenced work.

page 6942 line 24: how are the wet aerosol from the chamber dried and how do you

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know they have been fully dried? There does not appear to be an RH sensor on the polydisperse inlet to the first DMA.

page 6943 line 1: I am not sure what is meant by the statement 'a closed loop recirculation was used for the sheath flow in (the) DMA in order to avoid (the) problem of stabilizing RH'. The recirculating flow system will suffer from heating and still requires an active RH control system, just as an 'open loop' DMA flow control system with RH control would. How specifically does the recirculating system avoid RH fluctuations?

Also related to the above - why are there three blowers and three filters in the sheath flow recirculation line in the system schematic of the HTDMA? Please discuss the RH and temperature measurements in the upstream DMA. Also, there needs to be some discussing of the sizing performance of the HTDMA - results of dry ammonium sulfate selection by the upstream DMA and examples of scans by the downstream DMA under dry conditions showing good transfer function behavior and sizing agreement. PSLs could be used to demonstrate sizing accuracy.

page 6943 line 27 : how does the +/-2% RH fluctuation and the +/-3% RH measurement uncertainty translate into growth factor uncertainty? For example, what would the range of growth factors be for ammonium sulfate for 90% +/-5% RH?

page 6944 line 18: This sentence makes it sound like the SMPS, OPC and nephelometer were all controlled to the same RH as the chamber as the chamber RH was increased from 0 to 100% over the one hour period. Is this correct? Was the RH of each instrument actively controlled to match the current chamber RH as the RH was changing? Please clarify which instruments did and did not have RH control and the exact sampling conditions of each instrument.

page 6945: in the method to derive the complex refractive index, it is fairly clear how the method works for a purely scattering aerosol like ammonium sulfate with a homogeneous chemical composition with particle size. The scattering coefficient is measured, the size distribution is measured and the composition as a function of size, and there-

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fore refractive index, is known for the test aerosol. It is less clear, however, how this method would work for an aerosol population with size-dependent chemical composition (and therefore refractive index) since the Mie calculations would need to know the refractive index as a function of size to accurately retrieve Qscat. An even more difficult problem to deal with, it would seem, would be an internally mixed scattering and absorbing composition, where again, the composition and therefore complex refractive index could vary with particle size. Please explain how the method will be extended to these more complex circumstances representative of future conditions in the chamber. It is not clear that there are enough constraints to converge on valid real and imaginary refractive index values for more complex aerosol systems.

page 6945 line 21: how is the RH controlled within the nephelometer to allow comparison between measured scattering coefficient and integrated, humid SMPS size distributions? Please add a description in the text.

page 6946 line 3: How is the RH controlled within the OPC to allow proper sizing at the relevant RH? Wouldn't this be necessary to intercompare the SMPS and OPC distributions? What is the RH at which the optical sizing is performed within the OPC? Please add description to text.

page 6947 line 10: If the humidity in the nephelometer is reduced because of the 2 deg C heating, then isn't it the case that the scattering coefficient measurement at the lower RH cannot be set equal to the scattering coefficient calculated from the humidified SMPS measurements? Since particles of different sizes could reduce their size by different amounts inside the nephelometer due to the drying, it seems the measured scattering is not the same as that that would be derived from the SMPS distribution at higher RH.

editorial comments:

page 6939 line 25: particles should be particle

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page 6940 line 3: this work does not describe so much a new method as it presents results from a new experimental setup that is similar to that used by other groups (for example, Caltech, Aida chamber, other smog chambers around the world) - I would use the word 'new experimental system' and not 'new method'.

page 6940 line 11 should read: and an efficient scatterer of solar radiation

page 6948 line 18: this sentence doesn't make sense as written

page 6970 - the figure caption has an extra 'of' after the Duplissy reference

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 6935, 2013.

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