

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.

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We would like to thank to reviewers for their helpful comments which surely ameliorate the quality of the paper. We realize that we omitted a number of important details on the experimental conditions and this led to a very severe misunderstanding of the interpretation and relevance of our results. We apologize for this. We have taken these comments very seriously into account to overcome these shortcomings.

We have also worked very hard to improve the quality of the writing in order to help the clarity.

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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 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.

From the review provided by the reviewer 2, there is a clear disagreement between us about the conclusion we proposed based on our observations. We believe that at least a part of this disagreement is due to a lack of information about our experimental set-up / protocol.

Before any further discussion about our observations and the theories that support or contradict our conclusions, it is of primary importance to state some key experimental characteristic of our experiments:

1. Particles were highly dried before their humidification: A diffusion dryer was installed between the atomizer and the simulation chamber and particles were additionally dried during their mixing into the chamber with very dry synthetic air. The RH in the chamber remained below 1% RH before humidification.
2. There was no humid / cold spot in the chamber and in the sample line: In order to avoid any RH inhomogeneities within the chamber, great care has been taken to inject the water vapor slowly and continuously. To evaluate the homogeneity of the

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RH in the chamber, water vapor was introduced step by step in order to obtain various level of constant RH, lasting at least 15 minutes. The stainless steel fan installed inside the chamber mixed the reacting mixture throughout the whole chamber volume. Temperature and relative humidity were measured at different points of the chamber with various sensors, previously intercalibrated. It was observed equal reading (within error bars) of the sensors, indicating the homogeneity of the T/RH was obtained in less than 1 minute. During the experiments of ammonium sulfate particles, the T/RH were measured at different points of the experimental setup with three sensors: inside the chamber, at the inlet of the nephelometer and the inlet of the SMPS. We observed no increase of the RH or decrease of the T between the chamber and the instruments.

3. There was no water vapor release from filters / hot point in the humidification system of the SMPS: The factory-built hydrophilic filters in the sheath flow circuit were replaced by hydrophobic ones to avoid water vapor release. The sheath flow of the SMPS was humidified at the same RH as the aerosol sample flow to avoid RH gradients in the DMA by passing through a multiple-tube Nafion conditioner and monitored with another capacitive RH sensor placed in the circuit of the sheath flow. A heat exchanger was located at the exit of the sheath flow to equilibrate the temperature due to the compressive blower heating.

4. There was no shift response to the film capacitive RH sensors due to VOCs exposure: No VOCs were used during these experiments. Furthermore, all capacitive RH sensors were calibrated before the experiments. The DMA used for SMPS measurements during humidification in the chamber is the same as the second DMA of the HTDMA. Thus, RH sensors installed in the aerosol sample, sheath, and excess air of the DMA are also the same as those used during HTDMA measurements. HTDMA measurements agree well with theory and other studies using HTDMAs. Thus, no shift in RH sensors response was found.

All the possible care about this set-up has been taken as we were the first suspicious scientists about our results. More than 18 months have been dedicated to the improve-

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ment of this set-up and we are now really confident about its robustness. We believe that it has now to be confronted with the existing theories.

The reviewer notes that the HTDMAs were efficient to determine the deliquescence point for years and hence that there was not any problem in their operation. In addition, it is also claimed that the GFs as seen by HTDMAs are in good agreement with the Köhler theory. We want to clear state here that we obtained the same results with our two instruments (nephelometer and SMPS during in-situ humidification). Furthermore, we also obtain GFs in agreement with the literature / theory from the in-situ humidified aerosol experiments.

The novelty is the observed growth below the deliquescence point. This is clearly not in agreement with HTDMA measurement but this is probably related with very different processes which may involve adsorption over crystals. The equilibrium of the adsorption of water to particles should be governed by the adsorption isotherm (such as Langmuir, BET or FHH isotherms as described by Romakkaniemi et al., J. Phys. Chem. A, 105, 8183-8188, 2001), instead of Köhler theory that assumes deliquesced aqueous droplets.

The reviewer 2 is suspicious about our observation and assumed that some experimental problem could have led to the humidification of a part of the aerosol. We have already given our point about the experimental care taken. But if we consider reviewer 2's hypothesis, two remarks can be done:

1. The humidification of a part of the aerosol would have certainly led to two or more modes (which is not seen) or at least to a broadening of the distribution which is not seen either (Figure 8 in the article).

2. During the humidification process between 30-70%, the aerosol exhibits a growth far from several of the GF observed (from 1.03 to 1.11), which can not be attributed to any of the deliquescence or efflorescence curve and whatever the RH considered (figure S1 in the reply).

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We understand that these results are peculiar but we believe that future work may bring explanation and theory. We call for reproduction of these experiments that we believe to be important and so we believe it is important to have these data available for the community.

Below, we provide a point by point response to the other questions, comments and suggestions of the reviewers #2. Questions are reported in bold characters.

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

We agree that the complex refractive index was retrieved in this study only for purely scattering particles. Nonetheless, a spectral aethalometer (Magee Sci) was connected to the chamber to measure the light attenuation between 370 and 950 nm, so to retrieve the particle absorption coefficient. In the case of ammonium sulfate particles, the measured attenuation, after correction for the spurious signal due to particle scattering, and other artifacts as described in Weingarten et al. (2003) and Collaud-Coen et al. (2010) for absorbing particles, was nil as expected. The imaginary part of the refractive index was therefore set to zero.

We therefore believe that this experimental protocol, coupling aethalometer and nephelometer measurements, and including the correction procedure can be applied to absorbing particles to yield the imaginary part of the complex refractive index. We plan future measurements to test this hypothesis. Also, we are working to overcome the limitations of our current experimental protocol, which is to date limited to dry conditions (due to the limitation of the aethalometer) and to one wavelength only regarding to scattering (due to the limited spectral resolution of the nephelometer). For sake of

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clarity, a description of the retrieval of the measured absorption properties has been added to the paper (paragraph 3.1.1).

> 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

References have been added in the text

> 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 sentence means that the RH control is facilitated by the close loop recirculation since the sheath flow is already humidified at the exit of the DMA column (and so at the entrance of the sheath flow). The sentence has been change in the article by "a closed loop recirculation was used for the sheath flow in the DMA in order to facilitate the RH control".

> 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.

There are three blowers because the humidified DMA is an adaptation of the TSI DMA 3080, which used initially three blowers to provide a laminar sheath flow. Filters were used to obtain a free particle air. No RH and temperature measurements were made in the first DMA. These parameters were controlled in the simulation chamber and the

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RH within the chamber was always <1% during the HTDMA measurements.

The two DMAs of the HTDMA were calibrated using monodisperse PSL particles ranging from 100 to 500 nm. Size shift was observed for the two DMAs and thus a correction was applied for the retrieved diameters. DMAs were also intercalibrated before each HTDMA measurement by selecting different diameters with the first DMA and scanning the resulting size distribution with the second DMA. An example of resulting number size distributions is shown in Figure S1 of the Supplementary material. The retrieved diameters with the second DMA agreed with the selected diameters with the first DMA, therefore no more correction was applied to the DMAs diameters. A description of this HTDMA calibration has been added in the article.

> 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? The reviewer is right: the variability of the measured RH and the error on the RH measurement will impact the resulting growth factor measurements. However, we do not agree with the reviewer on the estimate of the amplitude of this effect as the $\pm 1\%$ RH fluctuation is actually masked by the $\pm 3\%$ RH measurement uncertainty so they do not sum up. So we have estimated the uncertainty on the size growth factor at 90% RH due to an error of $\pm 3\%$ for RH by using the theoretical calculations (Biskos et al. (2006)). We obtain 1.73 ± 0.24 at 90% RH, that is 13% relative uncertainties.

We have included this additional factor in the paper to illustrate the dispersion of the GF values.

> 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 therefore refractive index, is known for the test aerosol. It is less clear, however,

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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 system.

In the article, the complex refractive index has been determined for an internally mixed homogeneous spherical particle and thus Mie scattering calculations for homogeneous spheres were used to retrieve the refractive index. Should the mixing state or the composition be size-dependent, additional measurements of the particle composition would be needed to precise the model to be used for optical closure studies. The chamber is equipped with additional ports to sample aerosols on filters and size-segregating impactors. These samples can be analyzed by various techniques available in our laboratory, including scanning and transmission electron microscopy to yield the particle composition at the individual particle level, and their mixing state, including few-nanometer coating. Adaptations are also foreseen to yield the measurement of particle scattering and absorption as a function of size by mounting a size-selection device and a switching valve at the entrance of the instruments.

We also have the possibility of adapting the optical calculations. For an aerosol with a core-shell mixing, the homogeneous coated sphere theory presented by Bohren and Huffman (1983) can be used, whereas for more complex type of mixing the theories of Bruggeman or Maxwell-Garnet apply (Bohren and Huffman, 1983). In the case of an aerosol externally mixed, particles can be split up into size-classes (for example by using an impactor) before the measurement of their scattering and absorption coefficients. Thus, the complex refractive index as a function of the particle size (and

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chemical composition) can be determined, which allows to determine the aerosol complex refractive index.

> 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.

The complex refractive index was only retrieved under dry conditions. The RH was controlled within the simulation chamber, and at the entrance of both the nephelometer and the SMPS and showed a $RH < 1\%$. We clarified this point in the 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.

The decrease of 2 degrees in the nephelometer cell leads indeed to a decrease of the RH, which results in a decrease of the scattering coefficient. So, the scattering coefficient was measured at RH smaller than those detected at the entrance of the nephelometer. This is the reason why we calculated the RH within the cell of the nephelometer (see equation (12)) to know the correct RH the scattering coefficients were measured.

For the complex refractive index, calculations were only made under dry conditions. So, there is no problem for comparing SMPS distributions and nephelometer measurements.

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editorial comments: > page 6939 line 25: particles should be particle

The correction has been made

> 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'.

It has been changed.

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

The correction has been made

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

The sentence has been rewritten

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

The correction has been made

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

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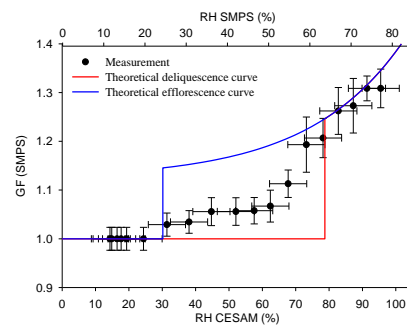


Figure S1. Hygroscopic growth factor GF as a function of RH within the chamber (bottom axis) and the RH within the measuring instrument (upper axis) obtained for the experiment E1212. The measurements (black circles) are compared with the theoretical growth factors based on the Köhler theory for deliquescence (red line) and efflorescence (blue line). Theoretical curves take into account the Kelvin effect for particles smaller than 100 nm.

Fig. 1.

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