Overview:

Alroe et al. describe a method for measuring the hygroscopicity of aerosols which separates the contributions of semi-volatile and low volatility components. Their approach combines measurements from an Aerosol Mass Spectrometer (AMS) and a Volatility and Hygroscopicity Differential Mobility Analyser (VH-TDMA), which together provide information about composition and hygroscopicity. The use of a thermodenuder (TD) allows the comparative impact of semi-volatile aerosol species to be assessed.

Overall the manuscript is interesting and within the scope of AMT. My major concern relates to data quality: while the extension compared to previous work is that the technique provides size-resolved (around 100 nm) and time-resolved data, the composition measurements do not appear sensitive enough to make this feasible in practice. Since all ambient and a large proportion of laboratory AMS measurements are reported to be below detection limit at this size range, it is not clear under what circumstances the full approach described is actually applicable to atmospheric measurements, or lab experiments. The authors therefore need to better justify their methodology and clarify the limitations of averaging over size bins and smoothing. I have some additional queries related to the analysis methods and overall clarity of the experiment descriptions which should be addressed before the manuscript is considered for publication.

General comments:

Experimental description: Many more details are required as to how the chamber experiments were performed (section 2.5): For instance: How much n-butanol was added? How was RH introduced, and what purity of water was used? How was the HONO prepared and introduced? Was the chamber mixed? How was the chamber cleaned? What were the background concentrations (particles, AMS, CIMS…) prior to the experiment?

Data quality: The authors admit in section 3.1 (P7 L10-14) that using highly time-resolved and size-resolved AMS data result in "unstable" data "often falling below the detection limit", even for lab experiments. If Fig 3 is a typical time series for the size range studied (130-180 nm), these concentrations seem more than sufficient for confidence in the AMS data. What is the source of this instability, then, and what is the size and origin of the background signal used to estimate the LOD? Can individual error bars be marked on in Fig 3? Without a more detailed discussion here it is difficult to be confident that the technique is viable and the results presented are meaningful in terms of quoted uncertainties.

Smog chamber experiments – aerosol dynamics: The authors note the rapidly changing conditions in the smog chamber experiments. However, substantially more information is required to understand the time series presented (Fig 3, 5-7). For instance, it is not clear how the aerosol mass loading ($\mu g/m^3$) and size distribution

($dN/dlogD_p$) actually evolve through the experiment – please present these as a function of time. It looks from Fig 5(a) that there are multiple maxima in the mass distribution – is this also the case in the number distribution, and if so why for a seeded experiment?

Related to this, one of the main driving forces for the rapidly decreasing HGF over time at 100nm is a decrease in sulfate, which is not even mentioned in the text. What are the causes of this? Can particle coagulation and wall loss rates be quantified, for instance?

I cannot reconcile the composition time series in Fig 3 and 5b. For instance, at 150 minutes in Fig 3, the sulfate and LV organic mass concentrations are comparable, while in Fig 5b, virtually no sulfate is present. I am wondering if Fig 3 presents the total AMS concentration rather than the size-resolved data as implied. If so its inclusion should be justified and thoroughly clarified. It would be necessary to see the raw size-resolved data also plotted and discussed in the context of “Data quality”, above.

Smog chamber experiments – derivation of HGFs: I have a number of queries about how the smog chamber hygroscopic growth factors were derived (P8 L1-22). Firstly, the ammonium sulfate HGF = 1.58 ± 0.03 from calibration experiments is low compared a range of previous measurements and the E-AIM and AIOMFAC models (1.7-1.8) e.g. (Denjean et al., 2014; Lei et al., 2014). Please discuss this discrepancy and how it might propagate given that AS is the dominant hygroscopic component.

The contribution of LVOA is estimated based on a parameterisation of O:C vs HGF from Massoli et al. (2010). However, the authors cite recent work suggesting O:C may not be a good proxy for CCN activity and hygroscopicity. They also find the two OA components in their experiments have similar O:C. Why, then, was this parameterisation used? And more problematically, why only for the LVOA? The SVOA HGF was estimated via a residual approach, whereas the parameterisation would give the same HGF as LVOA.

What value for HGF_{LVOA} would be obtained using the same approach as SVOA, i.e. calculating a residual HGF in the heated sample after the sulfate contribution is accounted for? Would the model perform substantially less well with a single HGF_{OA}, as is used for the ambient samples? Given the combined uncertainties in HGF_{LVOA} and HGF_{SVOA} (which overlap), and different estimation methods, the conclusion that the two fractions have different HGF needs to be better supported.

Specific comments:

P1 L20-22: Please provide a general reference for this paragraph.

P1 L27: Clarify what is meant by “dynamic nature” – many volatile species are not particularly reactive or prone to condensation/evaporation. Perhaps indicate specific species of importance.

P3 L15: Replace “the two instruments” with “the two instruments (AMS and VH-TDMA)”.

P3 L17: When is additional drying required? Was it required in any of this work? If not, delete.

P3 L26: The “Line A and B” terminology is confusing and is subsequently not used a great deal. According to Fig 1, A/B are not constant sampling lines but relate to the changing paths of the TD and unheated aerosol samples. Why not just use “TD” and “unheated” and remove “A/B” altogether? Similarly, for the wall-loss experiments (Fig 2), the exact path difference being monitored should be clarified.

P3 L30-31: Was this “stepping” performed here? If so, for which parameters?

P4 L1-2: What is the combined flowrate required, and hence the diluting flowrate? Given the interest in semivolatile partitioning, how was dilution of the gas phase accounted for?

P4 L8: “…all measurements were performed on aerosol with dm = 100 nm…”. This may be the case for all VH-TDMA measurements, but this is in the composition section and the AMS sample is not pre-classified according to Fig 1. Size-dependent number concentrations (Fig 4) and composition (Fig 5a) data are also shown later. Please clarify.

P4 L10: “If the aerosol is strongly size dependent”. Should this read “aerosol composition”?

P4 L18-19: Was this linear correction factor applied to any data here? If so, which?

P4 L20-24: Which data were smoothed in this study? Mention here and in corresponding Fig captions. Please define “LOESS”.

P4 L26-P5 L5: I am surprised that a Kelvin correction is required for a dry diameter of 100 nm. What was the magnitude of the correction?

P5 L30: Please change to “…transmission efficiency decreased linearly with increasing temperature…”.

P6 L12: Justify precision of [OH] – what is the uncertainty?

P6 L16: The mention of Fig 3 here, without discussion, confuses section 3.1 of the results. I suggest this Figure is not mentioned until it is discussed in the results.

P6 L30: Again, reference to “all measurements” is confusing here. For instance, Fig 4 shows time series, not 6-hour averages.

P7 L24: SVOA and LVOA are defined “for convenience” based on desorption at 120 ^{o}C. How does this threshold relate, approximately, to well-known measures of volatility, such as saturation concentration/vapour pressure, for the mass loadings used here?

P7 L26: Please provide a plausible mechanism or literature precedent for dark SOA production in these conditions. The method section also implies the seeds and RH were added prior to alpha pinene, rather than in the 30 minutes afterwards.

P9 L1: Could organosulfates also contribute to this volatile sulfate (and organic) signal?

P9 L9: The heated particles lost 12% of their volume, but apparently around 50% of their mass (Fig 8). Please explain this discrepancy.

Technical comments:

Fig 3: Please label the panels (a), (b) and (c) respectively and refer to them as such in the manuscript.

Fig 4 (b): The dynamic range of the colour scale tops out at ~10 cm^{-3} to my eyes. Please adjust, or bin the data rather than using a continuous scale.

Fig 5 (a): Please add the units of dM/dlog(dva).

References:

Denjean, C., Formenti, P., Picquet-Varrault, B., Katrib, Y., Pangui, E., Zapf, P. and Doussin, J.-F.: A new experimental approach to study the hygroscopic and optical properties of aerosols : application to ammonium sulfate particles, Atmos. Meas. Tech., 7, 183–197, doi:10.5194/amt-7-183-2014, 2014.

Lei, T., Zuend, A., Wang, W. G., Zhang, Y. H. and Ge, M. F.: Hygroscopicity of organic compounds from biomass burning and their influence on the water uptake of mixed organic ammonium sulfate aerosols, Atmos. Chem. Phys., 14, 11165–11183, doi:10.5194/acp-14-11165-2014, 2014.

Massoli, P., Lambe, A. T., Ahern, A. T., Williams, L. R., Ehn, M., Mikkila, J., Canagaratna, M. R., Brune, W. H., Onasch, T. B., Jayne, J. T., Petaja, T., Kulmala, M., Laaksonen, A., Kolb, C. E., Davidovits, P. and Worsnop, D. R.: Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles, Geophys. Res. Lett., 37, L24801, doi:10.1029/2010GL045258, 2010.