

Interactive comment on “A technique for the measurement of organic aerosol hygroscopicity, oxidation level, and volatility distributions” by Kerrigan P. Cain and Spyros N. Pandis

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Review by Fred Brechtel

General comments:

A more appropriate title would be: A technique for the measurement of organic aerosol cloud nucleating potential, oxidation level, and volatility distributions. Hygroscopicity is more generally connected with measurements made below 100% RH using an HTDMA or some similar tool.

Why limit the method to only organic aerosol?

C1

Please add a short discussion in the introduction section of the application of the technique to unknown composition ambient aerosol.

Techniques where multiple aerosol properties are determined simultaneously can be made much stronger by adding size resolution – e.g. by pre-selecting a time sequence of monodisperse particles with a DMA upstream of the various instruments, more easily interpretable data would likely result. This very likely, in part, explains the largely inconclusive previous studies as noted on page 4 line 15-20. Although beyond the scope of this work, I highly recommend the authors consider modifying their setup so a DMA is positioned upstream of the thermodenuder/bypass so all instruments sample the exact same monodisperse aerosol after having undergone the exact same thermal (or no) pre-treatment. This configuration will also help eliminate the ambiguity in the data comparison between aerodynamic diameter measured by the AMS and the electrical mobility diameter measured by the DMA and delivered to the CCN and CPC. Admittedly, the time resolution of the measurement will be sacrificed, but the much easier to interpret data and interesting size-dependent results that would be produced could be very exciting.

Consider the following thought experiment considering an unknown composition ambient aerosol. As configured, the AMS samples the polydisperse particle distribution after a certain temperature exposure in the TD. Any number of originally differently sized particles could contribute to the AMS response at a single aerodynamic diameter depending on the volatility distribution of the input aerosol to the TD. In fact, if some of the input aerosol to the TD were soot (or some other non-volatile species) coated with volatile SOA, the AMS may not detect the non-volatile core left after treatment in the TD. The scanning DMA and CCN systems would detect the presence of the non-volatile core, but there would likely not be a corresponding signal in the AMS. How would these results be interpreted? This situation is one where selecting monodisperse aerosol upstream of the TD would greatly facilitate interpretation of the measurement results.

C2

Most volatility studies assume that material volatile at or below the thermodenuder temperature setpoint is evaporated to the gas phase. However, it seems that chemical reactions stimulated by the high temperature environment may also change the composition and oxidation state of the particles within the TD. Can you comment on the likelihood of this?

Another general question worth asking is: what is the relevance of volatility studies to the atmospheric aerosol since they are never exposed to most of the temperatures used in TD studies?

Finally, it is not very clear to me why volatility would necessarily be well connected to hygroscopicity.

More detailed comments:

Page 2, line 10: suggest adding that the gases can produce new particles AND condense on pre-existing particles.

Page 2, line 29: please clarify what 'this SOA system' refers to.

Page 3, line 34: is 'MFR' defined somewhere?

Page 4, line 4: suggest "...that the hygroscopicity of organic aerosol generally increases with ..."

Page 5, line 5: were flow mixers employed upstream of the two sample flow splits to ensure the AMS/DMA and CPC/CCN received the same aerosol populations?

Page 6, line 20: please explain how 'mass fraction remaining' in the TD is determined using SMPS measurements. How is the density measured to convert the mobility volume distribution to a mass distribution?

Page 7, line 4: it is worth mentioning here the shorter residence time you expect at your maximum TD operating temperature.

C3

Page 7, line 4: please comment on the expected range in residence time within the TD. For the low flow rate and large tube diameter, do you expect laminar flow conditions? If so, wouldn't particles traveling near the centerline experience a residence time roughly half those near the walls? If this is the case, how would this impact your results?

Page 9, line 1: please explain what C^* means

Page 9, line 15: I am confused by the statement that using the 1D-VBS allows for comparison of different TD studies regardless of TD operating conditions. If the physical residence time in a TD is too short to allow complete volatilization, or if the temperature-time history within a TD is not represented by the temperature setpoint of the study, how would a model allow successful intercomparisons of different TD study results?

Page 10, line 2: please add the supersaturation value set in the CCN instrument after activation diameter

Page 10, line 6: 155 ± 1 nm? This level of uncertainty or standard deviation in the measured activation diameter is a little hard to believe, you are reporting a size variation of only $\pm 0.06\%$. If you were to scan monodisperse 155 nm diameter PSL calibration particles 50 times and calculate the variation in the measured peak size, my guess is you would see higher intrinsic measurement uncertainty than 0.06% .

Page 10, line 10: or that chemical changes to the particles that occurred within the TD rendered the particles less CCN active...?

Page 10, line 15: You make a very good point here that trying to generalize relationships between volatility, hygroscopicity/cloud activity and oxidation level is over simplifying the situation. However, it would be extremely useful if such relationships could be developed, perhaps by dividing organic species into certain families or structures with key similarities. Any comments?

Page 11, line 10: can you comment briefly on how you would extend this analytical approach to unknown composition ambient aerosol? E.g. mixtures of insoluble material,

C4

soluble inorganics and soluble SOA?

Page 11, end of page: missing period

Page 13: in performing the sensitivity analysis – did you systematically eliminate each one of the 18 equations and run 17 studies? Or did you just run one study after picking a single equation to eliminate?

How would your sensitivity results change if you ‘randomly’ added + or – one standard deviation to the experimental data used to constrain the equations? What if you added one standard deviation to all of your data?

Page 13, line 17: suggests

Page 14, line 2: if the method has difficulty with low concentrations, does this impact its usefulness for studies of the ambient aerosol?

Page 14, it would be helpful if you rewrote the paragraph starting at line 6 so it was easier to understand.

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