

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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General comments:

We would like to thank Dr. Brechtel for all his constructive comments and suggestions.

(1) *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 percent RH using an HTDMA or some similar tool.*

We can see the point, but one could also argue exactly the opposite: measurements

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of CCN properties are better for the quantification of the hygroscopicity of a compound given the non-ideal solution effects often dominating behavior below 100 percent RH. Given that it is clear that the hygroscopic parameter κ estimated in this method is κ_{CCN} we would prefer to keep the same title. To avoid any confusion we clarify now both in the Abstract and the Conclusions that the hygroscopicity is based on CCN activity.

(2) *Why limit the method to only organic aerosol?*

The method can be easily applied to inorganic or mixed aerosol populations. However, given that the volatility and hygroscopicity of the major inorganic aerosol components in the atmosphere is well understood, the organic aerosol is the primary focus of this work.

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

We have added the corresponding paragraph.

(4) *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*

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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.

This is an excellent suggestion. Adding size resolution measurements can enhance our results significantly. As with any experimental setup, there are trade-offs. By adding size resolution, we will lose time resolution, but use of both modes of operation is certainly possible in laboratory experiments that can be repeated. Additional challenges may include the characterization of the resulting low aerosol concentrations by the AMS. However, this approach could provide significant advantages in the interpretation of the results for ambient measurements. We will try to explore this idea in future work.

(5) Most volatility studies assume that material volatile at or below the thermodenuder temperature set-point 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?

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There is always a possibility that chemical reactions can occur in the TD and this is one of the main weaknesses of this approach. In this study, however, the likelihood of chemical reactions occurring is relatively small because the temperature in the TD never rises above 125°C. This is a relatively low value compared to most TD studies. A second test is based on the relatively small changes of the particulate phase composition (based on AMS measurements) as the temperature is increasing. However, none of these tests is conclusive. A detailed characterization of the composition of the remaining organic phase is required to quantify the contribution of reactions to the observed changes. This important point has been added to the Conclusions of the paper.

(6) 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?

The major advantage of the volatility studies based on TDs is that they provide insights about the less volatile organic components. These are usually in the particulate phase at room temperature, but they may evaporate partially at higher atmospheric temperatures or when diluted significantly. The least volatile secondary components, when created by gas-to-particle conversion processes are important for the formation and growth of new particles in the atmosphere. Finally, the evolution of the volatility distribution of the organic aerosol can provide an indirect way to gain insights about the very difficult to measure chemical composition and evolution of these thousands of components. This discussion has been added to the introduction of the paper.

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

This is an excellent point. It has been assumed that the bridge connecting these two properties is the oxidation level. It has also been proposed that the link may be so

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strong that knowledge of the oxidation level may be sufficient to determine both properties. Our work here, among others, suggests that this is not so straightforward and these linkages are quite complex and may be even non-monotonic.

More detailed comments:

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

Done.

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

It refers to the α -pinene ozonolysis SOA system. We have changed this in the manuscript.

(10) *Page 3, line 34: is 'MFR' defined somewhere?*

We have added a definition for MFR the first time it appears.

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

Done.

(12) *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?*

We did not use flow mixers. The streams were split using a normal T union. We have clarified this in the manuscript.

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(13) *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?*

To calculate the MFR, we divided the TD mass at each SMPS measurement by an interpolated BP mass using the BP measurements before and after the TD measurements. We used a constant density of 1.4 g cm^{-3} for α -pinene ozonolysis SOA according to the recommendation of Kostenidou et al. (2007). We have updated the manuscript to include this information.

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

We have added this point.

(15) *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?*

We do expect laminar conditions with a Reynolds number around 10, which would mean that particles traveling near the walls have longer residence times than those near the centerline. The effect of the simplifying assumption of an average residence time has been considered by Cappa (2010). The change in MFR when the more detailed fluid dynamics model was used was a few percent. So its effect on the results of the present study in which the volatility is characterized using logarithmically spaced bins is small.

(16) *Page 9, line 1: please explain what C^* means.*

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C* is the effective saturation concentration used in the 1D-VBS. We have added an explanation and the corresponding reference in the manuscript.

(17) *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 set-point of the study, how would a model allow successful intercomparisons of different TD study results?*

As stated in the introduction, thermograms are heavily influenced by several factors (OA concentration, particle size, residence time, etc.) and TD studies use different experimental conditions. This can result in quite different thermograms for the same aerosol even when the same TD is used. So use of a model simulating the aerosol evaporation inside the TD can help “translate” the measurements to the same basis, the aerosol volatility distribution. The 1D-VBS is a good framework for this analysis, but of course other descriptions of the aerosol volatility distributions are possible. We have rewritten this section to make it clearer as to why we recommend using a model to generate volatility distributions to compare between studies.

(18) *Page 10, line 2: please add the supersaturation value set in the CCN instrument after activation diameter.*

Done.

(19) *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 +/-0.06 percent. If you were to scan monodisperse 155 nm diameter PSL calibration particles 50 times and calculate the variation in the measured peak*

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size, my guess is you would see higher intrinsic measurement uncertainty than 0.06 percent.

This is a valid point and it is probably a coincidence for these data points. The standard deviation of the various activation measurements was a few nanometers. To avoid misleading the readers about the overall variability of our measurements, we do not show in the main text the variability in this specific case, which is a lot less than the average. The variability of all the measurements is shown in the corresponding figures.

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

We have added this to the manuscript.

(21) *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?*

This could be very helpful in determining useful relationships for families of organic compounds. There are many different ways to divide the species, but one that is widely used is to group them using PMF. It has been shown that these groups (M-OOA, L-OOA, HOA, etc.) exhibit different properties and we could group them this way. For this specific work, since the OA is from one source, this method is not that useful. We hope to be able to develop such relationships applying the approach suggested here in more complex systems including of course ambient OA.

(22) *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, soluble inorganics and soluble SOA?*

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Our intention is to develop the method enough, so that it can be applied to ambient aerosol. However, we believe that the availability of real-time automatic instrumentation for the measurement of the size-composition distribution of the sub-micrometer ambient aerosol will allow us to work with known chemical composition (with the exception of the organic compounds). The analysis could use the known hygroscopic properties of the inorganic aerosol components and focus on the properties of the organics. There are a number of challenges including the determination of the size distribution of the refractory aerosol components that are not measured by the AMS (though the SP-AMS or the SP2 can help with black carbon), issues related to the mixing state of ambient particles, etc. Techniques like the Positive Matrix Factorization (PMF) could help to split the OA into a few components and then determine their corresponding properties. We have included a few lines in the manuscript on how the method would be applied to ambient aerosol.

(23) *Page 11, end of page: missing period.*

Added.

(24) *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?*

We have rewritten the beginning of the sensitivity analysis section to provide more clarity on how we performed this test. We systematically removed each one of the 18 equations and solved the resulting system 18 times. A more detailed uncertainty analysis would involve selections of values from the corresponding distributions of the various parameters, repeating the calculation, and estimating the distribution of the values of the resulting parameters. Perturbing one parameter at a time is a cheap way

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to do that. Selecting extreme values for all parameters may lead to an overestimation of the uncertainty (this combination is quite unlikely). We believe that our sensitivity analysis approach is adequate for its purpose, which that is to identify if one of the measurements is dominating the answer of the problem.

(25) *Page 13, line 17: suggests*

Corrected.

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

The “low” is used in a relative not an absolute sense here. We now clarify in the revised paper that the mass fraction of a volatility bin must be greater than 0.1 to allow the accurate estimation of the bin’s properties based on a single experiment. When multiple experiments are combined together, the method is able to accurately estimate the bins’ properties as long as there was enough material (more than 10 percent) from that bin in at least one experiment.

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

We have rewritten this paragraph to help make it clearer to the reader.

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