

## ***Interactive comment on “Measuring the atmospheric organic aerosol volatility distribution: a theoretical analysis” by E. Karnezi et al.***

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*The authors present a theoretical analysis of thermodenuder data and the challenges in deducing actual organic aerosol (OA) properties such as volatility distribution, accommodation coefficient, and vaporization enthalpy. Volatility is a crucial property of OA worth exploring in detail, and thermodenuders are a widely used tool for its assessment; the correct interpretation of these data is thus of high importance. One of the fundamental problems in thermodenuders is that with the residence times employed, most of the times equilibrium cannot be achieved, leading to significant uncertainties in the interpretation of MFR curves. Whereas the authors mention this particular issue several times, a detailed discussion is missing, but should absolutely be part of a theo-*

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*retical paper on the interpretation of thermodenuder data. In addition, the paper would merit from an additional round of reviews by the authors; some paragraphs should be written more clearly and focused, and some of the references seem to be incorrect. I thus recommend accepting it for AMT after major revisions, considering the following comments:*

#### *Specific comments*

**(1)** *P. 862, lines 7 - 12 ff.: Give information on residence times in the thermodenuders, since they highly influence thermograms/MFR curves. As you say, as particles evaporate, the vaporization enthalpy and potential mass transfer resistance is very important– however, the time spent at a certain temperature plays a huge role here.*

We have followed the reviewer's suggestion and added a paragraph in the introduction of the revised paper discussing the residence times used in various thermodenuder designs, their effects on the corresponding thermograms, and the issues related to the timescales for aerosol equilibrium under various conditions.

**(2)** *P. 862, line 21: Since you change the order of magnitude of the accommodation coefficient by 2, how is it so surprising that the volatility distribution changes by one order of magnitude?*

Please note that the accommodation coefficient in that study was varied by a factor of 20 (from 1 to 0.05) and the resulting volatility distribution was shifted by approximately one order of magnitude. The lack of proportionality is due to the nonlinear relationship of the mass transfer rate and the accommodation coefficient for the larger particles in that study that took place in a rather remote area. The particles were mostly in the transition regime for mass transfer.

**(3)** *P. 863, lines 6 – 8: See previous comments – this confirms again how important residence time and achieving equilibrium are.*

We agree with this point and we address it in a paragraph that has been added to the introduction (see also our response to Comment 1 above).

**(4)** *P. 863, lines 8 – 29; p. 864, lines 1 – 15: Here you start the discussion on residence times – however, I would start this discussion further up. Would reaching equilibrium allow quantitative interpretations of physicochemical/thermodynamic properties of a certain compound?*

We have restructured the material in the introduction so this material follows the general discussion of the importance of the residence time. If the system reaches equilibrium, the measurement (e.g., MFR) becomes independent of the evaporation dynamics and therefore the result does not depend any more on the effective accommodation coefficient. There have been a number of efforts to take advantage of this by performing laboratory measurements at very high concentrations or concentrating the ambient particles and thus reducing the timescales for achieving equilibrium. Under certain conditions this is possible but under others (e.g., low ambient levels) it is not. We have added discussion about these efforts to reduce the equilibrium timescales in TDs and allow measurements closer to equilibrium. Please note that our approach for the interpretation of TD measurements does apply to these efforts too.

**(5)** *P. 867, lines 11-16: Similar thermograms for compounds with different volatilities – do we have to conclude that thermodenuders are not very useful unless we reach equilibrium? How would Figure 1 change with increasing residence time?*

Thermodenuders under most conditions measure the evaporation rates of aerosol and therefore provide useful information. However, extracting additional information (e.g., volatility) from these evaporation rates is challenging and the interpretation of the corresponding measurements should be done with great care. We do propose here an approach to at least quantify the uncertainty of the corresponding parameters retrieved from the thermodenuder measurements.

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Our work suggests that the corresponding measurements are quite useful for the estimation of the effective enthalpy of evaporation. However, the decoupling of the volatility distribution and the effective accommodation coefficient is more challenging than it has been assumed so far. Characterization of the system close to equilibrium (either with the same thermodynamic if the equilibrium timescale is short enough or with additional measurements like the isothermal dilution) is needed. Alternatively outside information (e.g., about the effective accommodation coefficient) is needed to constrain the problem.

The two curves of Figure 1 start diverging when we increase the residence time. However, the residence times that are needed to separate these two systems (several minutes) are outside the range of residence times that can be achieved with currently available systems.

We have added discussion of the above points in the introduction of the revised paper.

**(6)** *P. 867, lines 17 – 27: why do you need pseudo-experimental data when modeling? Why not just use the red curve?*

This is an important point of the present work. If one assumes zero experimental error, then the optimization algorithm estimates (as expected) the correct parameters for the system. However, if one takes into account the unavoidable measurement uncertainty (due for example to the variability of the measurement conditions), the optimization algorithm can converge to solutions that are very far from the accurate estimate. This behavior is characteristic of systems with multiple local minima. We strongly believe that pseudo-experimental data (taking into account the experimental uncertainty) should be used in all tests of inversion techniques of various measurement approaches, because either way the accuracy of the corresponding algorithms may be seriously overestimated. This point is now stressed in the corresponding section of the paper.

**(7)** *P. 871, lines 9 – 11: I assume with number of measurements you mean the temper-*

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ature resolution – please specify here.

This is correct. We have added the required clarification.

**(8)** *P. 873, lines 10 ff.: This paragraph should be structured better and the results presented in a clearer way, so that it becomes more evident which conditions lead to better results/lower errors. A graph might help.*

We have rewritten the corresponding paragraph in the revised paper focusing on the conditions that lead to lower errors. Unfortunately, it is not possible to depict the corresponding complexity in a simple graph and therefore we have to rely on a Table in which the interested reader may find all the corresponding information.

**(9)** *P. 874, lines 15: So the residence time is still too short?*

Yes, the doubling of the residence time provides some information but in a lot of cases the system is far enough from equilibrium and the corresponding value of the additional information is a lot lower that we thought. Increases of the residence time by two orders of magnitude or more are often needed according to our analysis. This is very difficult in continuous flow systems so the use of a chamber is explored. We have added a couple of sentences in the end of this section clarifying this point.

**(10)** *P. 876, lines 7 -8: Since this is a crucial part of the paper, more information should be added on the combination of TD and isothermal dilution measurements. This is a very unspecific statement.*

We have added the requested details regarding the combination of thermodenuder and isothermal dilution measurements. Briefly, the same method as in Section 2.3 is used, treating equally the TD and isothermal dilution measurements in the estimated error (equation 10) and combining the results of the simulations of both types of experiments.

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*Technical corrections*

**(11)** *P. 860, lines 22 – 23: [...] influencing the properties and lifetime of clouds.*

We have followed the suggestion.

**(12)** *P. 862, line 17: respectively, not accordingly.*

Corrected.

**(13)** *P. 864, lines 20 – 21: Reference is missing in bibliography. Or did you mean to cite Vesala et al (1997), which use, however,  $\ln((1-\pi/p)/(1-\pi_0/p))$ ?*

We have added the reference in the bibliography.

**(14)** *P. 871, line 11: Reference is not in bibliography (or year is wrong).*

The year of the reference in the text of the paper was wrong (the paper was published in 2007). The An et al. (2007) in the reference list is correct.

**(15)** *Table 1: Repeat in the caption what the letters mean, especially Xi.*

We have added this information.

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Interactive comment on Atmos. Meas. Tech. Discuss., 7, 859, 2014.

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