

Interactive comment on “Characterization of a thermodenuder- particle beam mass spectrometer system for the study of organic aerosol volatility and composition” by A. E. Faulhaber et al.

Anonymous Referee #1

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This is an ambitious paper that addresses an important topic. The goal is to develop an instrument to measure the volatility distribution of ambient organic aerosols. This was done by coupling a particle mass spectrometer with a thermodenuder. The system was calibrated using single component particles generated from compounds with "known" vapor pressures. The system was tested by applying it to two more complicated mixtures. All of the experiments were performed at high particle concentrations (100s of $\mu\text{g}/\text{m}^3$).

Overall I think that this is an important paper and should be published in AMTD after the authors have addressed the following comments.

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Big picture comments.

This is an empirical approach because they are calibrating the system using compounds with known vapor pressure. The advantage of this approach is that it avoids a lot of uncertain parameters such as accommodation coefficients, enthalpies of evaporation, etc that are required to directly model/interpret thermal denuder data. This potentially makes it very attractive. However, there are some key assumptions underlying the approach that should be discussed in more detail. First, the approach is that the evaporation kinetics of single component particles are the same as complex particles. For example, the uptake coefficient does not vary with particle composition, etc. Second the paper requires calibration compounds with known vapor pressure. As noted in the paper, these data are available for a very small number of compounds, and the uncertainty in the data increases with lower vapor pressure. There are also essentially no data for very low vapor pressure compounds. This complicates developing robust calibration curves. These ideas should be more clearly stated in the manuscript (what problems it avoids, and what assumptions underlie the approach). This might fit in well in the intro and/or beginning of the methods section.

Page 21 "Considering the uncertainties in the literature values the agreement between the experimental distribution and the simulation output is otherwise quite good." I think that you may be relying too much on comparing the volatility distributions. These distributions are describing the gas particle partitioning of the mixture. Most likely there are a number of different volatility distributions that give basically the same overall partitioning behavior. Therefore I would recommend comparing how different the partitioning behavior is for these distributions (for example if you ran them all through your TD model and plotted M/Mo versus T). If the partitioning behavior for the different distribution is not that different means that the actual volatility distribution is not well constrained by the data. There is a recent paper by Stanier et al. in AE (2008) that discusses this issue (uniqueness of fits).

A key to making this work as a technique to characterize the volatility of ambient aerosol

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is that the thermal denuder must be calibrated at atmospherically relevant conditions (concentrations and diameters). The paper uses a model to examine the effect of these concentration and diameter (Figure 7). A concern is that most of the work was not done at atmospherically relevant concentrations, which may bias your estimates – given the empirical nature of the approach it would probably have been better to do the work at atmospherically relevant concentration. Page 13 provides an estimate of the maximum potential error associated with the effects of variable particle size and concentration (a factor of 9). The paper says this error is acceptable given the other uncertainties. That seems to be a reasonable assertion given the uncertainty in vapor pressure of calibration compounds, etc. However, calibrating the system with high particle concentrations (a factor of 10 or more than typical atmospheric levels) creates a systematic bias because reducing the concentration always lower the T50. This bias is quite substantial for smaller particles. Can the calibration curve be corrected for this bias? It seems like it would have been much better to calibrate the system with 10 ug/m³ of aerosol as opposed to 200. Although this error might now seem that large for some configurations, for others it could influence the derived volatility distribution. It seems advantageous to try to eliminate any known systematic errors from the approach.

More minor comments

Page 2 "volatility behavior" Not sure what you mean by this. Presumably a better word might be description of gas-particle partitioning. This phrase is used in a number of places in the manuscript.

Page 6. "background signal" What was this background signal due to? (I was thinking gas phase organics that were not completely removed by vacuum pump). How big is the correction? What is the uncertainty associated with this correction?

Page 8, Tinf .. How was this determined?

Bottom of page 12 or presumably longer residence time would increase mass loss if

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the system is not in equilibrium.

Modeling – it would be good to more clearly state that the aerosol is not in equilibrium at the end of the TD therefore you are using a dynamic model to interpret the data.

Page 12 "good agreement" not sure what is meant by this. You appear to have reduced the effective residence time for 15 to 6.5 sec? What is the justification for this change? If you changing parameters to improve fits it is not clear you can claim good agreement.

Equations 2 and 3 – I did not see an accommodation coefficient in these equations. Recent work suggests that the accommodation coefficient of complex aerosols is not one (see Stanier et al. EST 2007 reference in this manuscript). Also the variables immediately following equation 3 in the text did not seem to be defined (adding a nomenclature list to the end of the paper would be helpful).

Does the modeling account for any evaporation in the denuder section?

Following equation (4) what is the τ ? 6.5 seconds?

Given the size dependency of the evaporation rate, should the thermal denuder be always operated with a monodisperse aerosol? Ie put a DMA upfront as was done for the calibration experiments? Or does this create S/N problems for the MS.

Page 17 " C^* corresponding to the ambient temperature" I do not understand this. Presumably it gives you C^* up to around the initial concentration of the organic aerosols – for example if you have 10 $\mu\text{g}/\text{m}^3$ of aerosol TD allows you to probe the volatility of material with C^* of around 10 and lower (ie the material that is in the condensed phase).

Page 22 – Discussion of Figure 11. "The volatility distribution predicted for this SOA sample after a 10-fold dilution" This was confusing. The volatility distribution does not change with dilution (unless the chemistry has changed). What is changing is the concentration of the species and the gas-particle partitioning.

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Section 3.8 – This section seemed to come from left field. The paper is long and complicated enough already. I would recommend deleting this section.

Figure 7 – This figure was not well labeled. The solid lines correspond to continuum model. There are four lines – presumably corresponding to different particle diameters. This was not clear. Which line corresponds to which? Same comments for free-molecular lines. Maybe make this figure in color?

Bottom of page 19 and Figure 9. "True distribution" and "do not follow the behavior expected from their vapor pressures" Not sure if this is the really true distribution given the uncertainty of the P_{vap} values in the literature. The C18 uncertainty is approaching a factor of 10. Could the issue instead be uncertainty in literature vapor pressure as opposed to non-ideal solution effects?

Figure 11. You are inferring volatility distribution down to 10^{-4} ug/m³. This is at least two orders of magnitude lower than the least volatile (and most uncertain) of the calibration compound. What is the uncertainty in extrapolating your calibration curve?

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