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Atmospheric
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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.

A. E. Faulhaber et al.

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Responses to Referee Comments

We would like to thank both referees for their generally favorable reviews, and for constructive comments. We have prepared a revised manuscript incorporating most of these comments. We address all specific comments below.

Responses to Anonymous Referee #1 Comments

Comment 1.1: 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.

Response 1.1: We agree that summarizing these advantages and limitations and presenting them clearly is important. The following summary has been added at the end of the introduction (pg. 4, line 4 in the revised manuscript):

"The technique avoids many of the difficulties that would be encountered if modeling, rather than an empirical relationship, were used to extract vapor pressure distributions from the data. These include the need to have an accurate model of the detailed dynamics of the system and the need to use various properties of the particles and constituent compounds as input when even the identity of the compounds in the sample is unknown. It does, however, implicitly assume that these properties are adequately well represented by the particles of standard compounds used to calibrate the technique. Besides simple molecular parameters and particle properties such as size, shape, and mass concentration, these may include factors such as differences in evaporation coefficients, changes in evaporation coefficients with temperature (particularly if phase changes occur in the mixture), the mixing state of the particles, and the presence of oligomers or other unstable species that may undergo chemical changes with temperature.

In addition, the technique can only give results as good as the vapor pressure data used in the calibration, and accurate vapor pressures for low volatility compounds are scarce. This introduces some additional uncertainty, especially for vapor pressures below the range covered by the calibration, for which extrapolated values must be used (although vapor pressures far below the calibration range are less important, as material with these vapor pressures will generally be found almost exclusively in the particle phase). Despite these limitations, it is shown that vapor pressures can be estimated to within one order of magnitude for a variety of samples."

Comment 1.2: 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).

Response 1.2: The question seems to be to what extent different actual volatility distributions can lead to similar measured volatility distributions. The distributions in this figure (Fig. 8 in the revised manuscript), when used as input for the TD model, all produce significantly different output, and this can be predicted from examination of the distributions and the discussion in Sect. 3.5 of factors that influence the measured distributions. While it does not pertain to this point directly, we have softened our claim about the agreement between the simulation output and the experimental distribution from "quite good" to "fairly good," since we noticed that the differences between the

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simulation output and the experimental distribution can be explained largely by a shift of ~0.5 orders of magnitude in *C**. This is discussed further in Response 1.19. However, the question of uniqueness of actual distributions leading to a given measured distribution is still a good one. To some extent the discussion just mentioned in Sect. 3.5 answers this question, although not explicitly. The following explicit discussion of this topic has been added to the end of Sect. 3.5 (page 20, line 22 in the revised manuscript):

"It should be noted that the factors discussed above–the broadening due to the TD vaporization profile width and the fact that the measured vapor pressure for a component in a mixture depends on the mass fraction as well as the actual vapor pressure–imply that the true volatility distribution is not uniquely defined by the measured distribution. For example, all else being equal, a distribution with 10 μg m^{-3} in the *C $=$ 10^{-1} μg m^{-3} bin and nothing in the higher volatility bins will give roughly the same measured distribution as one with 9 μg m^{-3} in the *C** $=$ 10^{-1} μg m^{-3} bin and 1 μg m^{-3} in the *C** $=$ 10^{0} bin due to broadening. Similarly, a mass fraction of 5% in a bin at the low volatility end of the distribution can give the same intensity in the next-to-lowest volatility bin as a mass fraction of 10% in the next-to-lowest volatility bin because a lower mass fraction at this end of the distribution is shifted more to the higher volatility side. These are extreme examples, but these factors should be borne in mind when interpreting measured volatility distributions. A similar issue has been discussed recently by Stanier et al. (2008) with respect to the parameterization of volatility data from chamber experiments."**

Comment 1.3: A key to making this work as a technique to characterize the volatility of ambient aerosol 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 T_{50}. 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.

Response 1.3: Relatively high mass loadings were used in this study due to the lower sensitivity of the TDPBMS relative to that of the AMS or similar mass spectrometer (as stated in Sect. 1, the TDPBMS is used in this study as a surrogate for such a mass spectrometer). As pointed out in Sect. 3.2, differences in temperature profiles between individual TDs should be expected to effect the calibration, and it is our opinion that investigators using this technique will probably want to carry out calibrations themselves in order to account for this. This is stated explicitly in the revised manuscript, in Sect. 3.2, paragraph 1 (pg. 10, line 22 in the revised manuscript): **"Therefore, in order for P_{25} to be estimated accurately using this technique, separate calibrations should be carried out for individual TDs."** We have expanded upon this point to include recommendations on particles to be used in these calibrations. Specifically, we have changed the discussion on calibration at low mass concentrations to recommend an appropriate particle size, and removed the argument that such a calibration is not necessary. The addition in Sect.3.3, last paragraph (pg 15, line 4 in the revised manuscript) reads:

"For calibrations to be used for ambient studies, therefore, the choice of particle size is important. From Eqs. 4 and 5, it can be shown that $T_{50}{}^{-1}$ is roughly linear with respect to logd_p. Therefore, the mean of the mass distribution with respect to logd_p expected for an ambient study along with a typical ambient mass concentration are ideal for calibration of a TD."

Comment 1.4: 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.

Response 1.4: We agree that this term is used in several places as a synonym for gas-particle partitioning, and that the later is much more precise. Therefore the term has been replaced with "gas-particle partitioning" in those cases. There are 3 instances in Sect. 3.6 paragraphs 2 and 3 (pg. 21, line 28, pg. 22, line 3 and 21) in which "volatility behavior" seems to be an appropriate term, and in those cases the meaning is clear from the context, and term has not been replaced.

Comment 1.5: 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?

Response 1.5: Factors known to contribute to the background signal are listed in Sect. 2.3, paragraph 2 (pg. 7, line 6 in the revised manuscript). The uncertainty in the background varies greatly with the aerosol. Rather than discuss the range of uncertainties from the background or attempt any kind of quantitative estimate, we have added a note to the effect that it is a major contribution. The text incorporating these changes reads:

"The background signal, which arises from gas-phase species which are not completely removed by the pumping system, material slowly leaching from the vaporizer coating, and material from the particle beam that does not vaporize promptly (probably because it is deposited on other surfaces within the mass

spectrometer), was measured by setting the DMA voltage to 0 for monodisperse aerosols (so that no particles exit the DMA), or by placing a Teflon filter in the line upstream of the TD for polydisperse aerosol and SOA. Since background variability was a major contribution to the uncertainty in M_T/M_0 for some of the systems studied, the background was measured frequently during the experiment, and the appropriate value to subtract from the signal at any time was estimated by interpolation."

Comment 1.6: Page 8, Tinfl .. How was this determined?

Response 1.6: This information has been added in Sect. 3.1, paragraph 2 (pg. 8, line 28 in the revised manuscript): **"T_{infl}, the inflection point in the TD vaporization profile, corresponds to the peak in the aerosol mass evaporation rate, and is approximated here by the maximum in $-d(M_T/M_0)/dT_{TD}$ after smoothing."**

Comment 1.7: Bottom of page 12 or presumably longer residence time would increase mass loss if the system is not in equilibrium.

Response 1.7: This is true. The fact that equilibrium is not reached in the TD is addressed in our response to the next point.

Comment 1.8: 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.

Response 1.8: A note to this effect has been added in Sect. 3.3, paragraph 1 (pg. 12, line 7 in the revised manuscript):

"Since it cannot be assumed that the particles reach equilibrium in the TD in all cases, dynamic models for two mass transport regimes were used in the simulations."

Comment 1.9: 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

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for this change? If you changing parameters to improve fits it is not clear you can claim good agreement.

Response 1.9: We do not claim that the simple model used in this study accounts for all the complexities of the actual dynamics of evaporation in the TD, and we have clarified this point in Sect. 3.3, paragraph 1 (pg. 13, line 7 in the revised manuscript) and listed some details that were not included in the model:

"The model is not intended to reproduce all the details of particle evaporation in the TD, such as the longitudinal and cross-sectional variation in temperature and gas flow rate, and evaporation and re-condensation that takes place in the charcoal denuder region. Such details would be necessary if the model was being used in an attempt to determine molecular parameters by fitting experimental data, but for the present purpose of describing trends in the data, such a rigorous description of the system is unnecessary."

Given the details not included in the model, not to mention the uncertainties in those included, it would be surprising if the model did agree with the experimental data without the adjustment of any parameters. The model results agree well with the data, and capture the trends in T_{50} with changes in particle size and mass concentration, which we believe is enough to justify a qualitative discussion of particle evaporation in the TD based on this model.

Comment 1.10: 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).

Response 1.10: In Response 1.1, we have addressed the issue of the accommodation (or evaporation) coefficients of complex aerosols. The model is used in this study for a pure compound in one case, and a mixture for which our intent was to model ideal behavior in another case; hence, we believe that setting the evaporation coefficient to 1 in Eq. 2 and ignoring the Fuchs-Sutugin correction factor including the evaporation coefficient in Eq. 3 is justified. The effect of changing these assumptions on the model results is now briefly mentioned in the Sect. 3.3, paragraph 1 (pg. 12, line 21 in the revised manuscript): **"It should be noted that reducing α from 1 to 0.3 in Eq. 2 or including the Fuchs-Sutugin correction factor (Seinfeld and Pandis, 1998) with an evaporation coefficient of 0.2 in Eq. 3 has a similar effect to reducing the effective residence time."**

Comment 1.11: 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).

Response 1.11: We have added a nomenclature list as Appendix A.

Comment 1.12: Does the modeling account for any evaporation in the denuder section?

Response 1.12: No. This is explicitly stated in the revised manuscript along with some other details not included in the model (this addition is quoted in Response 1.9). As explained above, the model is not intended to treat all the details of the system.

Comment 1.13: Following equation (4) what is the tr? 6.5 seconds?

Response 1.13: Eq. 4 is not used for any numerical calculations, only for qualitative discussion. Since it may not have been clear in this paragraph (Sect. 3.3, paragraph 3) that the model referred to in all cases is the continuum model, this is clarified in the revised manuscript. Specifically, we have changed "this model" to "the continuum model" on pg. 13, line 24, and specified that the ratio of T_{50} values in Fig. 6 referred to on pg. 14, line 12 is for the continuum model.

Comment 1.14: Given the size dependency of the evaporation rate, should the thermal denuder be always operated with a monodisperse aerosol? Ie put a DMA up front as was done for the calibration experiments? Or does this create S/N problems for the MS.

Response 1.14: We believe the error incurred by using a single calibration for a typical range of ambient particle sizes is acceptable, as explained in Sect. 3.3 in the original manuscript. Under some circumstances, size-selecting particles for ambient measurements might be useful, and a size-specific calibration could be done for the particular size of interest. Generally, however, this would limit the usefulness and ease of implementation of the technique. Scanning over sizes *and* temperatures in an ambient study is not likely to be practical.

Comment 1.15: 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 ug/m3 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).

Response 1.15: The following note has been added in Sect. 3.5, shortly after Eqn. 13 (pg. 19, line 1 in the revised manuscript): **"If the calibration is done at a mass concentration close to the concentration of the aerosol being sampled, this should be essentially C_{OA}."** Because use of the calibration requires the assumption that mass concentration is not important to T_{50}, the point at ambient temperature corresponds to the C* which should give 50% evaporation at ambient temperature (obviously, only the derivative, and not the actual value of M_T/M_0, has meaning here; the signal when the TD is bypassed only includes 50% of material that is 50% in the condensed phase).

Comment 1.16: 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.

Response 1.16: We agree that this was a poor choice of words. "Volatility distribution" has been changed to "partitioning by volatility bin."

Comment 1.17: 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.

Response 1.17: Part of the purpose of using mass spectral detection in conjunction with the TD, as stated in the introduction, is to get some information on composition as a function of volatility. This section demonstrates that. It doesn't add much to either the length or the complexity of the paper. Therefore, we prefer not to delete it.

Comment 1.18: 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?

Response 1.18: Fig. 7 (now Fig. 6) has been changed to show simulation results for different particle sizes in different colors.

Comment 1.19: 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 Pvap 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?

Response 1.19: From Fig. 9a (now Fig. 8a), it can be seen that the C18 and C20 monoacids and oleic acid have essentially the same vaporization profiles in this mixture. Even if we assume that the uncertainties in the vapor pressures are enough for any one or even two of these compounds to have a true vapor pressure corresponding to this vaporization profile, the difference in vapor pressure for two compounds in a homologous series with a difference of two in the carbon chain length should be enough that the behavior shown here can be labeled non-ideal with some confidence. We have, however, changed the discussion of Fig. 8b so that we no longer imply that the non-ideal behavior leads to an overall bias in the low volatility bins, as mentioned in Response 1.2. The revision to that discussion in Sect. 3.6, paragraph 3 (pg. 22, line 30 in the revised manuscript) is as follows:

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"Overall, the simulation output is shifted to lower volatility than the experimental distribution by $\sim$0.5 orders of magnitude in *C. It is not clear whether this is due to a bias in literature vapor pressures or other factors. The non-ideal behavior described above, in which the three lowest-volatility components vaporize at essentially the same temperature, may contribute to this difference, but it may only have the effect of smoothing the low volatility side of the distribution."**

Comment 1.20: Figure 11. You are inferring volatility distribution down to 10710;-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?

Response 1.20: Extrapolating the uncertainty in P_{25} would be difficult since we don't know all the factors that contribute to it. Rather than attempt to make a quantitative estimate of the uncertainty, we have added a reminder in Sect. 3.7, paragraph 2 (pg. 24, line 3 in the revised manuscript) of the increase in uncertainty with extrapolation which was pointed out in Sect. 3.2: **"it should be noted that the values of P_{25} and *C** in Figs. 9 and 10 extend below the range covered by the calibration by about 3 orders of magnitude, and the uncertainty at these lower volatilities, as discussed in Sect. 3.2, is necessarily greater than it is within the calibration range."**

Responses to Anonymous Referee #2 Comments

Comment 2.1: p5: the used CPC probably is a 3010 (not 310)

Response 2.1: The CPC model is 3010, and this correction has been made in the revised manuscript.

Comment 2.2: The flow rate into the MS should be given

Response 2.2: This information has been added in Sect. 2.4, paragraph 1 (pg. 7, line29 in the revised manuscript): **"The aerosol is sampled through a 0.1 mm critical orifice, which results in a flow rate of $\sim$0.075 l min^{-1}"**

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Comment 2.3: An explanation for the 16K difference between T_{des} and T_{infl} would be interesting

Response 2.3: The following explanation has been added in Sect. 3.1, paragraph 3 (pg. 9, line 15 in the revised manuscript):

"The temperature offset is primarily due to the difference in evaporation timescales for the two techniques. In TPTD analysis, T_{des} is typically reached in ~5 min for the standard temperature ramp rate of 2^{o}C min^{-1}. In TD analysis, T_{infl} is the temperature at which approximately the same fraction of the particle mass evaporates in the ~10 s transit through the TD. In order to compensate for the much shorter time available for evaporation in the TD, the particle vapor pressure must be higher, which requires that T_{infl} be higher than T_{des}. A more quantitative analysis of the effects of particle properties and measurement parameters on this temperature difference could be carried out using the evaporation models employed here for the TD and the one used previously for modeling TPTD evaporation (Chattopadhyay and Ziemann, 2005)."

Comment 2.4: Fig.5 can be removed, as all information is also included in Fig. 6.

Response 2.4: Figures 5 and 6 have been combined.

Interactive comment on Atmos. Meas. Tech. Discuss., 1, 21, 2008.