

Response to reviewer comments for manuscript: “On the calibration of FIGAERO-ToF-CIMS: importance and impact of calibrant delivery for the particle phase calibration”

Ylisirniö et al.,

We thank the reviewer for his/her constructive comments regarding our paper. Below we will address the specific issues point by point. The reviewer's comments are in black and our answers are in blue. Changes to the Manuscript or Supplement Information are highlighted in red. Line numbers before the red response text refer to line numbers in the modified manuscript.

Additional changes by authors:

We added additional discussion about potential effect of collected aerosol mass loading to Section 3.3.

Line 281:

“An additional aspect that has been reported to shift T_{max} values is the amount of collected aerosol mass on the PTFE filter (Huang et al., 2018), becoming important when collected particulate mass is around several micrograms. We tested the mass loading effect by collecting different amounts of atomized PEG's up to 200 ng of mass and found no clear difference between measured T_{max} values (data not shown). However, as collected aerosol mass on the FIGAERO filter can easily reach microgram amounts, especially when sampling in highly polluted environments and as we did not rigorously test how T_{max} values behave above 200 ng, we suggest that this effect is investigated further in future publications.”

Reviewer 3:

GENERAL

Modeling (Page 6, 3rd paragraph; page 7 last lines; page 8, 3rd and last paragraphs, page 11 1st paragraph): The model brings enough insight to justify itself for the paper, but I think it could be better tied to the results. As the model predicts the effect of particle diameter, maybe this aspect could be dealt with first. One could estimate the surface to volume ratio of the residue to that of the fitted 11 μm diameter particles. It seems that an order of magnitude agreement would be achieved with a reasonable residue thickness estimate. Another thing: why is the model insensitive to particle diameter for PEG-8? The authors might like to check for papers that have come out after preparing the manuscript.

We believe that the storyline works well enough as it is, and it is more in line with how our understanding progressed during this study. We first had the observation of increased desorption

temperatures for syringe methods, and blaming that on reduced S:V was one of several initial hypotheses, but the one that crystallized as the most plausible explanation. Our evaporation model is able to simulate that effect, in its simplifying approach, but nonetheless able to roughly quantify it, so we agree that the obtained numbers are providing useful “ballparks”. (The SEM pictures were then taken last.)

Estimating the S:V of the residue, based on the SEM pictures, is an interesting approach – if very qualitative only, as the “reasonable residue thickness estimate” is a major uncertainty. But if we anyway, for example, looking at Fig. 5, maybe a good guess would be a residue consisting of $20 \times 20 \mu\text{m}^2$ blocks with a depth of $1 \mu\text{m}$? The corresponding S:V is $2.2 \mu\text{m}^{-1}$, equivalent to the S:V of a sphere (particle) of diameter $2.7 \mu\text{m}$. Indeed, a reasonable order of magnitude agreement is achieved (the model using $1.3 \mu\text{m}$; Fig. 4). But a major problem remains with the lack of depth information obtainable from the SEM images, as up to the filter thickness ($\sim 150 \mu\text{m}$), a suitable residue thickness can mostly be found (“estimated”) to come up with the particle size value desired. Indeed, one could argue that, vice versa, SEM images plus modelled particle size could be used to estimate residue thickness. Adding to that argument are the similarities regarding apparent residues between Fig. 1 panels a) and b) in this document above, despite different solution concentrations used (0.01 and 0.25 g/L, respectively), whereas the model would use particle sizes of 1.3 and $>11 \mu\text{m}$, respectively (Fig. 4). But if we keep with $20 \times 20 \mu\text{m}^2$ patches, we only need to increase their depth, for example to $5 \mu\text{m}$, and the corresponding particle size would increase to $10 \mu\text{m}$. Voilà. So those calculations are able to provide reasonable numbers. That is encouraging, but we feel that they remain poorly constrained by our observations (plus model simulations), and we do not learn much more, and only with high uncertainties.

Regarding PEG-8/Fig. 7, please see response to Reviewer 1, comment 10.

Regarding the new papers that have been published during the review progress, we have added Wang et. al., (2020) calibration line to Figure 1 and Figure S2.

SPECIFIC COMMENTS

Abstract:

There would be room for specific numbers on the effects of the methods on peak temperature, pressure and concentration.

Added an example about the difference in T_{max} between atomizer method and syringe method and how big effect this would cause in C^* space.

Line 22:

“For example, we found a difference of $\sim 15^\circ\text{C}$ in observed T_{max} values between the atomizer method and the syringe method when using the lowest solution concentration (0.003 g L⁻¹). This difference translates to up to 3 orders of magnitude difference in saturation concentration C^* space.”

Methods:

Page 4 and onwards: I understand the concentration probably affects the residual ring pattern, but it would be nice to also show the deposited solute mass.

Deposited solute masses are already being reported in the end of the Sect. 2.3. “The mass deposited varied between 9 ng and 500 ng, depending on the used concentration.” In the SEM pictures amount of deposited mass was 30ng. This information is now added to the figure caption.

Eq (3) and related texts: C^* -space is referred to later in the text several times, as is customary to the field. On the other hand, this paper (or the supplement) does not provide the physical properties of the compounds needed to convert the saturation pressure values to concentrations. Including the equation is therefore of limited value. Maybe the properties could be listed in the supplement? Or then just point out here that this is a linear function. BTW: molecular weight/mass should be changed to molar here, and later when appropriate.

If the reviewer refers to $P_{sat, meas}$ or M_w as physical properties of the compounds, the $P_{sat, meas}$ value is determined from measured T_{max} value using eq(2) and M_w is determined directly from the CIMS data. This is now clarified in the text and molecular weight is changed to molar mass.

Line 164:

“where M_w is the molar mass of the compound (in units of g mol^{-1}) determined with the CIMS,”

Results and discussion

Figure 3 and related texts: Overall this is a nice set, conveying the message. I have some minor points: -Please harmonize the two panes for marker and text sizes -There would be more room to spell out the Saturation vapor pressure within the caption than on the axis. This is shortened to Saturation pressure elsewhere in the text. -I guess the lines are just to guide the eye. Why are they missing from the b) and why is the PEG atomizer data included? -I propose checking (dashed) horizontal lines to the P_{sat} values -Please refer to supplement here for the P_{sat} values -I did not find mention of the sources of the carboxylic acid P_{sat} values. These should be added.

Figure 3 is now modified as requested. Used P_{sat} values for carboxylic acids and their reference are listed in Table S1 and this is mentioned in the text.

The lines connecting the dots in Fig. 3a) are indeed to guide the eye. They are however missing from Fig 3b) from carboxylic acids as the data is more compacted and thus would make the figure harder to read. Also, the PEGs are a homologous series, whereas the acids are not. The PEG atomizer data is included for easier comparison between the two panels as the x-axis is different in each panel.

Figure 5: The scale bar text is too small. Although is implicitly clear, maybe the caption should spell out that this is after solvent evaporation. Maybe use the word residue?

Increased the scale bar text and added fourth panel as suggested by Reviewer 1. New panel shows zoomed in picture of panel a). Changed the word ‘PEG-8 “ring”’ to ‘PEG-8 residue’.

Figure 6: I know there is little that can be done here, but it is practically impossible to tell the particles apart from the filter. The marked particles are approximately one micrometer in diameter, not 300 nm. Any explanation?

It is indeed hard to distinguish the collected particles from the filter material. We base our estimation on the quantity of the white “blobs” seen in the picture with deposited particles compared to the clean filter. The amount of material collected onto the filter was substantially higher than what would be normally collected during experiments, to ensure the identification of the particles from the filter material. It is possible that some of particles have coagulated in the filter and formed bigger particles.

Page 8, last paragraph and figure 7: Explain what the difference in the inlet was, and why it affects the T_{max} values.

The other inlet used in this paper was a slightly modified version from the general Aerodyne inlet. The two inlets differ geometrically slightly from each other in terms of pin hole and thermocouple positioning. However, as the point of the calibration is to ensure that different FIGAERO systems are comparable to each other, slight changes in the inlet geometry are not crucial. The largest source of error regarding T_{max} values comes from the exact positioning of the filter thermocouple, which is individual to each FIGAERO inlet, and is an important reason to use harmonised calibration method between different FIGAERO instruments.

Figure 8: Nice result, but as this is calibration, should there not be an error estimate?

Error bars are now added to the figure and the error analysis is explained in the supplement information.

Page 10, 2nd paragraph: “Note that the heating ramp rates in these calibrations were done with faster heating ramp rate...” This sentence can be shortened quite a bit. Apart from that, maybe the authors would like to discuss the effect of the ramp rate in the light of this paper...

We modified the sentence:

Line 317:

“Note that the calibrations shown in this paper used faster heating ramp rates than what was used in the SOA measurements, introducing an overall small systematic error (<1 order of magnitude in C^* space) towards higher saturation concentrations.”

The effect of the used ramp rate on the observed T_{max} values is discussed in Sect. 3.3, last paragraph, and the effect is shown in Figure 7.