

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 2

Major comment:

The manuscript deals with calibration issues, which means it deals with quantitative issues, and it compares to results from other references. Although the authors made aware of suited fitting procedures for data with errors in y and x (line 168f) there is no detailed error analysis nor are error bars shown in the Figures 1, 4, 7, 8, S2, S3. The only errors given are the statistical errors from averaging single measurements. I find that strange for a paper that deals with quantitative analysis and urgently suggest to add more detailed error analysis’ and -discussion.

The reviewer is correct that more detailed description about the errors is needed. The main results of the paper are the T_{max} value measurements, i.e. the actual temperature measurements and its associated errors. The FIGAERO inlet uses two k-type thermocouples, which have typical measurement error of +/- 2.2 K. Additional ~1K of error is also introduced by the electronics of the

measurement system. However, this total uncertainty of ~3 K can be thought of as a systematic error, rather than a random error. Therefore, the calibration procedure itself captures this uncertainty. Any random component of the temperature measurement error is then captured with repetitions and shown in standard deviations. An additional component to the error is introduced in the fitting of the asymmetric lognormal function over the measured thermograms. This error can be estimated by using the fitting routine's goodness-of-the-fit parameters, such as R-square value.

In Figures 1, and S2 the error bars are omitted for sake of clarity, but this is now pointed out in the captions and errors are discussed in the sect. 2.5.

Error bars and their description are now added to Figure 4 and explained in the caption.

In Figure 7, the error bars are omitted from the figures measured values as they are not distinguishable in the x-axis direction and do not add value to the plot. A range of the models results are however now shown in panel b) when using the uncertainties for evaporation enthalpy ΔH shown in Krieger et al (2018). The y-axis error values are the same as in Figure 4. The range of the errors is now given in the figure caption:

“Error bars are omitted from the measured values in the figure for sake of clarity. In the panel b) whiskers show the range of model results when using uncertainties of evaporation enthalpy shown in (Krieger et al., (2018). The standard deviations of the for all measured points is panel a) is between 0.2-0.5 °C. In panel b) the standard deviations for measured points are between 0.2 – 1.3 °C.”

For Figure 8 error bars are now shown in the plot and the error analysis is explained in the supplement information S4. Briefly, the x-axis errors are calculated with propagation of error for both syringe injections and aerosol collections. The Y-axis errors are estimated by assuming Poisson-type counting statistics.

In Figure S3 the error bars are not shown as the idea of the figure is to be mainly speculative on how the P_{sat} values of higher order PEG-compounds could possibly be estimated.

Minor comments:

line 44: References should be given already here, in addition to the link to section 2.5.

Moved citations.

line 82: Are these heating rates really so accurate (2 decimal digits)? The experiments do not lead to the same maximum temperature, does that effect the integrals under the thermograms?

We decreased the accuracy of the ramp rate to one digit. For the integration, the thermogram is integrated against time and not temperature, as data is measured in counts per second. Therefore, maximum attained temperature does not affect the integral value as long as it was high enough for all material to desorb from the filter.

line 97: From PEG-4 to PEG-8. In integer steps? Please, specify precisely which PEG's you used.

Text has been modified to mention all used PEG-compounds.

Line 99:

The used PEG standards were PEG-4, PEG-5, PEG-6, PEG-7 and to PEG-8.

line 115-120: Did you use a neutralizer ? If yes, which? How did you handle multicharged particles in the selection by DMA. This needs to be explained, and potential errors need to be estimated and discussed.

The TSI model 3082 SMPS-platform contains a Kr-85 radioactive neutralizer and the measurement software automatically corrects for multicharged particles. When used in DMA mode for monodisperse aerosols, the particle size was selected from the falling edge of the polydisperse particle distribution, keeping the amount of multicharged particles at a minimum. For example, the measured mode diameter of the polydisperse aerosol distribution was ~50nm and we selected 100 nm monodisperse particles for the sensitivity measurements.

Figure 6: I don't see a real difference between with and w/o particles. What made you think that the marked white blobs are particles? The marking with the red circles is too suggestive. I propose to leave them out. In this context: In the ambient with aqueous particles and RH, wouldn't the particles flow together and merge anyhow? I would still believe that even considering that, particle deposition should lead to finer structures compared to evaporating droplets deposited by syringe. What could be the influence of a fast evaporating solvent the structure of the dried deposit? Did you do experiments with others solvents?

The reviewer is right that it is indeed difficult to distinguish the PEG-8 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.

When considering aqueous particles, the distance between the collecting filter fibres compared to the size of the collected aerosol particles is large enough that the particles should not meet each other unless using very high mass loading when collecting the sample. The aerosol particles are also so small that intermolecular forces between the particles and filter fibres should be strong enough to prevent them from moving around in the filter by the collection flow drag. Note that for high sample mass on filters, sample mass dependent shifts of T_{max} have been observed (Huang et al. 2018, Atmos. Chem. Physics) which may be connected to particles interacting on the filter.

As the PEG-8 molecules are floating freely in the acetonitrile (ACN) solution without diffusion limitations, the evaporation rate of the solvent should not affect how the PEG-8 molecules deposit onto the filter.

As for other solvents, to dissolve PEGs a polar solvent is needed. However, we observed oligomerisation reaction for PEG4 when using alcoholic solvent (methanol). In addition to ACN we did test ethyl acetate and deionized water as solvents for both the syringe and the atomizer method but did not take SEM pictures with these solutions. We decided to use ACN instead of Ethyl Acetate as its less volatile. The higher volatility of ethyl acetate could have caused problems in

atomization as the atomizer solution concentration would have changed too rapidly as the solvent evaporates. Additionally, the PTFE-filter is less phobic towards ACN than it is towards water, which eases the syringe deposition experiments. For these reasons, we recommend using ACN as solvent for PEGs. However, if ACN is not available, it is possible to replace ACN with another aprotic/non-alcoholic, somewhat polar solvent at least in the atomizer method.

line 216 and Line 219: “We were largely able to reproduce our measurement results: : :” and “with practically no free parameters”, what do ‘largely’ and ‘practically no’ mean in this context, please, rephrase or specify.

We specified and tried to clarify those two sentences, now reading as follows:

Line 228 onwards:

“We were able to reproduce our measured T_{max} values within 10 °C using the evaporation model to simulate the evaporation of mixed PEG 4-8 particles (for simplicity assuming equal mole fractions for all PEG). For PEG-5 and -6, Figure 4 shows excellent agreement between measured and modelled T_{max} values for the atomizer method (within a couple of °C), deteriorating to a difference of about 10 °C for PEG-8. This broad agreement here is remarkable in so far, as in this case the model was run with no vapor-surface interactions, i.e. no tuning in regards to resulting T_{max} , which are therefore a direct result of the input values for C^* and ΔH .”

line 326-329: This statement should be appear in the result section before.

Moved the paragraph to Section 3.1.

Typos:

line 30: the these, cancel “the”

Done.

line 52: "stems“, turn to plural

Done.

line 62: Bannan et al. 2019, add the brackest to year

Done.

line 70: “that atomizer method”, add “the”

Done.

line 486(Figure 1): “for the further divergence”, didn’t you mean “larger divergence?”

Replaced with “large”:

“...for the large divergence...”

line S48: “d”, should be “f”

Done.