Interactive comment on “A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its application to chamber and field studies” by Thomas J. Bannan et al.

Anonymous Referee #1

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General comments:

The manuscript "A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its application to chamber and field studies" by Thomas J. Bannan et al. reports on well-executed experiments that succeeded well in calibrating the desorption heating of FIGAERO-HR-TOF-CIMS instruments. FIGAERO is a fairly novel technique that has started to gain wide-spread use recently and proven powerful in retrieving information on composition, volatility, and more, from organic aerosol particles. Therefore, I think that publication of this manuscript in Atmospheric
Measurement Techniques (AMT) will be very useful for the atmospheric science community. The authors describe their measurements well, and convinced this reviewer that they have been carried out properly and with due diligence. I recommend publication of this manuscript in AMT, however, following some minor revisions.

First, the title includes "application to chamber and field studies". However, I believe that application was only done to chamber experiments, so I suggest to remove the reference to field studies. (Although the method can certainly be applied to field studies, but if that is the intention to communicate, it may be better to reformulate.)

More importantly, a few parts of the manuscript are not as clearly described or as clearly discussed as I would prefer. And I think that some desirable information is missing regarding experimental details. I will discuss these issues in detail in the following.

Detailed comments:

Regarding the discussion of blank or background measurements (both for calibration and chamber SOA experiments, sections 2.2 and 2.4): Was there noticeable blank (=background?) signal, and was there a need for subtracting from data, or how where blank measurements treated?

p. 1, l. 55-56: Many LVOC and all ELVOC, probably very relevant for SOA, are typically considered to have much lower vapor pressures (e.g. Tröstl et al., 2016). (That is, referring to room-temperature saturation vapor pressures.) So I suggest revising that statement.

p. 3, l. 43: Does "inside" mean inside the heating block?

p. 3, l. 63: Do I understand correctly that the filter was replaced after the blank measurement? Why? More detailed description a few paragraphs below suggests that the filter was already new for the blank measurements and not changed thereafter, but not sure... Suggest reformulating. Better yet, combine, so that the filter handling procedure
is only described once.

p. 4, l. 10-15: I don’t understand the notation "200/300 °C". Later-on a heating to 300 °C is not mentioned again. (And wouldn’t PTFE start getting problems when heating that high? Or is the 300 °C referring to the temperature measured farther away from the filter?) Anyway, the heating rate (6.1 °C/min) and time (45 min) is consistent with 300 °C. I assume the equivalent heating rate for standard desorptions was (300-25)/10 = 27.5 °C? Maybe best if the authors could include that default heating rate, and clarify the issue regarding 200 vs. 300 °C.

p. 4, l. 27-32: The peak fitting procedure used for GU FIGAERO data appears quite complex. This paper is maybe a good place to present that procedure more clearly, e.g. by adding an explanatory figure that shows example data and the fits at various stages of the fitting procedure.

Section 3.1: According to section 2, 0.1 µL of solution were deposited during all calibration experiments. But it would be useful for the community to know also their concentration and the total mass of PEG that was deposited. That information could be included in Table 1, for instance. And please plot that fit (Eq. 1) also in Fig. 4. Regarding the data in Fig. 4: I feel there is a somewhat large variability in the observed Tmax values (if I think about my own experience with FIGAERO data). I would expect better reproducibility, in particular given that the PEG deposits are chemically simple and presumably identical in terms of amounts deposited for individual experiments and deposition technique. Do the authors have ideas what could have caused that variability?

Section 3.2: As commented above regarding section 3.1, please add information about the deposits in those experiment, e.g. in Table 2. And are the Tmax from single measurements or an average over several repetitions? Analogously, Table 3 should include the aerosol mass collected. There has been some indications that the amount collected can affect the observed Tmax (e.g. Huang et al., 2018). It could also be interesting
to know about the variability in observed $T_{max}$, as the listed values are the mean of 7 measurements. In general, the agreement between retrieved vapor pressures and literature values is convincing. But regarding the SOA experiments, I would have expected observed ("effective") vapor pressures to be much lower compared to pure-compound values, due to the Raoult effect (e.g. Donahue et al., 2006): I guess that the various acids reported here respectively only constitute a small fraction of the SOA (by the way, another piece of information that could be reported, in Table 3). Taking into account a Raoult effect would presumably worsen the agreements with literature considerably. I interpret that such that the evaporation from SOA is maybe not directly observed. Instead it might be vapor-pressure controlled processes that follow the initial SOA evaporation that somehow determine $T_{max}$. Interactions with instrument surfaces? Could that explain the large differences reported from different FIGAERO versions (Stark et al., 2017)? I am curious about the authors’ opinion on that. (And by the way, that Stark et al. paper should be cited in this manuscript. There isn’t too many reports of FIGAERO calibrations out there yet, and that is one of them.)

p. 5, l. 21: I think the authors mean $10^{-7}$ Pa instead of $10^{-4}$ Pa? (I agree with the use of $10^{-4}$ Pa in the next line though.)

p. 5, l. 62: There is some mistake in that first sentence. Besides, as mentioned above, I disagree that the PEG calibration compounds actually cover the full volatility range of atmospherically relevant organics. At least the specific PEG compounds used here.

Minor/technical comments:

p. 2, l. 8-10: double-mention of ongoing measurements, suggest mentioning only once for style

p. 2, l. 28: changes. Same in p. 3, l. 37-38, or maybe I am misreading these sentences.

p. 2, l. 30: "and" too much?
p. 2, l. 35: "," too much

p. 3, l. 26: I assume the GU CIMS was operated with either acetate or iodide reagent ions?

p. 3, l. 38: Definition of Tmax is inconsistent with its definition before (and again at p. 3, l. 48). Probably wrong use of "defined".

p. 4, l., 41: I find the sentence hard to follow

p. 4, l. 64: odd amount of brackets

p. 5, l. 20: unclear meaning of "extend"

References:


