

A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its application to chamber and field studies

We thank the reviewers for their time evaluating this manuscript and their positive comments relating to this work. The corrections and additions made as a result of these comments have greatly improved the consistency and focus of this work. The response to each point immediately follows each comment and is coloured red.

Anonymous Referee #1

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.

Detailed comments

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.)

Response: The paper title has been changed to: "A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its experimental application"

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 were blank measurements treated?

Response: for the calibration there was no background signal in each thermogram which needed to be analysed. A more detailed background procedure for the chamber experiments is now also included. However, given that quantitative concentration data is not reported, only the behaviour of the desorption profiles, there was no need for subtracting backgrounds from the data reported here.

"First, a new filter was placed in the FIGAERO and the temperature was ramped to 200°C for 10 minutes to ensure the filter was clean and then cooled. A ramp, soak and cool cycle matching that of the subsequent sample was then completed to obtain the filter background. In addition, and after the filter background, a chamber background was then taken daily that involved a 45 minute filter collection of air from the chamber with no VOC added and with no detectable particles in the chamber and subsequent desorption."

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.

Response: The filter used for the blank desorption was used for the following PEG experiment and this has been now better explained in the text. Sections 2.3 and 2.4 have now been switched for better flow of the experimental procedures.

“Prior to each sample measurement being made using both the GU and UMan FIGAERO-CIMS instruments, background measurements were obtained. First, a new filter was placed in the FIGAERO and the temperature was ramped to 200°C for 10 minutes to ensure the filter was clean and then cooled. A ramp, soak and cool cycle matching that of the subsequent sample was then completed to obtain the background. During the PEG series measurements the filter was ramped to 200°C (temperature above the filter) over a period of 20 minutes (at a rate of 8.75°C min⁻¹), held at 200°C for 10 minutes and finally allowed to cool back to room temperature for a period of 5 minutes. The same cycle was used for the single component measurements for both the GU and UMan instruments. It is however noted that the analysis provided here does not take into account the possibility of a change in ramp rate affecting the T_{max}. It is therefore recommended that the calibration cycles match that of the measurements. Temperature cycles and gas flows were controlled using the ARI EyeOn™ control system.”

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.

Response: That is correct – the sentence has been rewritten as;

“Functionalization can create compounds with a huge range of expected saturation vapour pressures between 0.1 Pa and 10⁻¹⁰ Pa and lower (Jimenez et al., 2009; O’Meara et al., 2014; Bilde et al., 2015, Tröstl et al., 2016).”

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

Response: as detailed in the text it relates to inside the copper tube, however to be clearer a link to Figure 2 is added where the position of the thermocouple in question is illustrated

“The gas temperature is measured by a 1/16” diameter thermocouple positioned inside and just near the exit of the ¼” OD copper tube (~5 mm above the PTFE Teflon filter as detailed in Figure 2).”

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?

Response: the notation was here to show that some desorptions during the experiments were run to 200⁰C and others to 300⁰C, but we agree that this is not clear. The hotter filter temperature and longer desorption times were used, as described in the text, to enable resolution of multiple peak desorptions and calculation of more accurate T_{max} values, but as all the results presented in this study are based on the measurements up to 200⁰C, references to the longer desorption and hotter temperatures have been removed as we agree that at 300⁰C the filters would likely not be thermally stable.

The position of the temperature that is measured is now also clarified in the text

“During the PEG series measurements the filter was ramped to 200°C (temperature above the filter) over a period of 20 minutes (at a rate of 8.75°C min⁻¹), held at 200°C for 10 minutes and finally allowed to cool back to room temperature for a period of 5 minutes.”

Maybe best if the authors could include that default heating rate, and clarify the issue regarding 200 vs. 300 °C.

Response: agreed. This has now been included.

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.

Response: A substantially expanded and improved description of the details of this method has now been included in the supplementary information for this paper.

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.

Response: the total mass and concentrations of PEG used in this study are now discussed in the following text:

“Four desorptions of each PEG were performed by depositing 0.1 μL of two different concentrations (two repeats of each), of $200 \mu\text{g cm}^{-3}$ and $2000 \mu\text{g cm}^{-3}$, with a mean of the 4 desorptions being reported as the T_{max} . No linear dependence of T_{max} with concentration was observed across this concentration range. As with any calibration it is recommended to use a comparable amount of calibrant material as would be expected to accumulate during the measurements, as it is noted that the amount of condensed material on the filter can affect the T_{max} . A range of calibration concentrations larger than that reported in this study is suggested for future studies and the small range is noted here as a limitation of this study. PEG calibrations were generally conducted individually and were manually syringed on to the filter. The reported T_{max} value for the one of highest concentration runs for PEG 4 and PEG 6 as well as PEG 5 and PEG 8 were mixed in two separate experiments. The conditions were designed to ensure that the T_{max} of the PEG series was not mixture dependent, although a more detailed study is required.”

And please plot that fit (Eq. 1) also in Fig. 4.

Response: this has now been added.

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?

Response: We have thoroughly checked all known parameters that may affect the thermograms reported here and whilst we recognise there is rather more variability than may be typical for FIGAERO calibrations we are unsure of the reason. In general, varying concentrations and ramp rates might potentially lead to varying desorption profiles; although in this study we did not perturb ramp rates and, with the concentrations used here we see no direct evidence of this. Given the variability between the past reported responses to VP and Tmax, as reported in Stark et al., (2017) the importance of calibrating individual instruments is reiterated, as many effects noted above can affect the thermograms.

Section 3.2: As commented above regarding section 3.1, please add information about the deposits in those experiment, e.g. in Table 2.

Response: As above, this has now been addressed.

And are the Tmax from single measurements or an average over several repetitions?

Response: The Tmax is a mean over 4 repetitions. This is now stated in the text in section 3.2 where the concentrations of each desorption are now also noted.

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).

The variability for the T_{max} during this experiment is now reported in table 3 as requested below. We see no relationship between the T_{max} and the total mass measured in the chamber, but we agree that this may be an important factor to consider, and is now discussed as below.

“As with any calibration it is recommended to use a comparable amount of calibrant material as would be expected to accumulate during the measurements, as it is noted that the amount of condensed material on the filter can affect the T_{max} . A range of calibration concentrations larger than that reported in this study is suggested for future studies and the small range is noted here as a limitation of this study.”

The range of total mass observed in the chamber during this measurement period to show that this has been considered in the caption of Figure 6.

It could also be interesting to know about the variability in observed T_{max} , as the listed values are the mean of 7 measurements.

Response: the maximum observed variability in the T_{max} from each of the 7 thermograms is now included in table 3.

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.

As we have already stated in the paper;

“This work also makes the necessary assumption that this filter-based measurement in an uncharacterized mixed matrix yields single component sub-cooled liquid VPs.”

And therefore the FIGAERO does not produce a mole fraction scaled vapour pressure. We assume that all components, even if they were originally associated with an aqueous solution when in the aerosol, will have precipitated out of solution according to their solubility as the water is driven off and then evaporate as “pure” components. Each compound therefore exhibits their pure component vapour pressure and it will not depend on their mole (or mass) fractions.

The ARI FIGAERO inlet used in this work is similar to that described by Lopez-Hilfiker et al. (2014), but not identical and differences in the position of the thermocouple position, flows and general configuration of the FIGAEROs will have implications for the reported T_{max} values from each instrument. This discussion is however outside the scope of the paper as we are presenting a method of calibration for each user and not the direct translation of results.

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.

Response: Agreed, this paper is now referenced several times throughout the revised manuscript.

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.)

Response: That is correct; this has been corrected in the text.

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.

Response: There was a mistake in that sentence, yes. This has been corrected with an amendment to show that this calibration does not cover the full volatility range of atmospherically relevant organics, but a very significant part of it. Amended to:

“Recent comparison of vapour pressure measurement techniques (Krieger et al., 2018) has identified the PEG series as a group of compounds that can be trusted as reference compounds for a range of measurement methods that across a wide range of tropospherically representative vapour pressures.”

Minor/technical comments

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

p. 2, l. 28: changes. Same in p. 3, l. 37-38, or maybe I am misreading these sentences. **Response:** change is the correct use here.

p. 2, l. 30: "and" too much? **Response:** this has been left as is.

p. 2, l. 35: "," too much **Response:** this has been left as is.

p. 3, l. 26: I assume the GU CIMS was operated with either acetate or iodide reagent ions? **Response:** this is correct and has been clarified in the text.

“GU CIMS was operated with acetate or iodide as the reagent ion.”

p. 3, l. 38: Definition of T_{max} is inconsistent with its definition before (and again at p. 3, l. 48). Probably wrong use of "defined". **Response:** yes, defined is the wrong use here. This has been change to “measured” in reference to the position that the T_{max} is measured.

p. 4, l., 41: I find the sentence hard to follow **Response:** this sentence has now been changed slightly.

p. 4, l. 64: odd amount of brackets **Response:** this has been corrected.

p. 5, l. 20: unclear meaning of "extend" **Response:** extend has been removed here

Anonymous Referee #2

General

To understand partitioning of (organic) substances in the atmosphere is a key issue. Recently FIGAERO CIMS was developed as a promising method. However to avoid misinterpretations of field and chamber measurements carefully characterization is needed. This manuscript clearly contributes to such a characterization. It addresses the derivation of VP from the conc. maximum of desorption curve in FIGAERO thermograms, utilizing a well characterized reference set of PEGs. The paper is interesting and compact and well written. I suggest publication in AMT after the authors addressed some minor points below.

Minor points

p217: I am wondering about the Ovadnevaite et al. 2017 reference in the context of gas-phase - particle phase partitioning.

Response: this has been removed from the text

p2130: What is the reason / are the conditions for observation of T_{max} ? And related: what is the physics behind the expected (Gaussian, p4147-50) shape of the thermogram? Schobesberger thinks of evaporating particles, but you seem to assume liquid states. Wouldn't the liquids spread and wet the filter fibers? I understand that those details are not really important for the results, but it may help to give an idea/introduction about your imagination of states and processes.

Response: the state of the material is discussed in reference to the comments of reviewer 1.

p3137: Something is wrong with this sentence. Please, check and reformulate.

Response: this has been completed

"The evolution of the MS signals from different compounds the filter is exposed to during the Temperature Ramp phase change independently as a function of temperature creating thermograms that are m/z specific."

p4113f: "200/300" I don't understand what is meant. 45 min x 6.1° will get you 275° on top of the RT of 25°, i.e. to 300°C. You may split and separate the info you intended to give into two sentences.

Response: this has now been clarified, as per the request of reviewer 1. Reference to the 300°C measurements have now been removed as no data from these measurements from these experiments have been used in the study.

p4129: I don't understand what you want to say here. How can subtraction of a background fit improve instrumental noise. I guess you have to extend here a little bit more.

Response: correct. In response to this and the comments of reviewer 1 a significant improvement in the details of this method has now been included in the supplementary information.

p4147: T_{max} for a fragment only reflects T_{max} of the parent compound, if the fragmentation happened after evaporation, i.e. in the gas-phase. However, as far as I understood, there could be also fragmentation - at weak bonds - in the particulate phase, isn't it? Then T_{max} of appearance of the fragment does not represent the thermal properties of the parent anymore. If so, you have to modify this statement in the manuscript accordingly.

Response: this is correct and should also be included. The following has been added to account for this;

"There also may be fragmentation of weak bonds in the particulate phase, also giving an unrepresentative T_{max} and desorption profile."

p5126: I suggest to include/show this fit in Figure 4.

Response: this has now been added.

Figure 3: Sample 1-3 were measured during the ramp. Sample 4,5 after the ramp stopped and the system stabilized (at a lower rate of t increase). Does the ramp rate have any effect on the T_{max} ? I guess so. But then sample 4,5, were not measured at same condition as sample 1-3. Please comment.

This variability is now noted in the text and is noted as a limitation in the study

“The same cycle was used for the single component measurements for both the GU and UMan instruments. It is however noted that the analysis provided here does not take into account the possibility of a change in ramp rate affecting the T_{max} . It is therefore recommended that the calibration cycles match that of the measurements.”

Figure 6, p4162: I don't understand what is shown here. In the chamber measurement you don't know if the detected formulas are the dicarboxylic acids as tagged? Or did you add the dicarboxylic acids as such. Please, clarify.

Response: measurements reported here are the dicarboxylic acids measured during the chamber experiments; this has been made clearer in the text now. These acids were identified through very low errors in the peak peaking and very high repeatability and gaussian shape of the thermograms.

“In addition to the PEG VP calibrations, we also performed FIGAERO measurements of secondary organic aerosols generated in the Manchester Photochemical Aerosol Chamber and vapor pressures of several organic acids (mass accuracy all <2 ppm) from measurements made in these experiments are reported here.”

Check co-author name "Krieger" vs "Kreiger"

Response: the manuscript has been thoroughly checked for this mistake and corrected

Check the use of capitals in figure, it should Figure

Response: this has been corrected throughout

Check the use of capitals in peg / PEG

Response: this has been corrected throughout

p2110: 'Such measurements "of are" ongoing. . .'

Response: this has been changes as per the comment of reviewer 1.

p319: maybe: "(> 6 month)"

Response: agreed

p4126: too many "averages" here

Response: agreed, the sentence has been rewritten as - *“The average (mean) of the maximum 3 values in the thermogram is used to extract the T_{max} values reported here.”*

p4149: "mass spectrometry and CIMS" is somehow double, you may want to modify this phrase

Response: correct. Mass spectrometry is deleted from the sentence to only leave reference to CIMS

p5118: "Tmaxes"

Response: this is the correct use here.

p7112: the "Foley" reference is incomplete

Response: this reference has now subsequently been removed from the main text

Anonymous Referee #3

The manuscript, 'A method for extracting calibrated ...' describes a method of using a series of PEG compounds to calibrate the FIGAERO for determining vapor pressures of detected compounds. The work presents a useful concept that can be used by a growing number of research groups that use the FIGAERO and similar techniques to normalize (or standardize) measurements of the volatility of OA components. The manuscript is succinct, which is nice, but some potentially major details are missing. Please address/clarify the below issues that may affect the applicability of the presented concept, after which the manuscript can be considered for publication.

Specific Comments

A series of PEG compounds was used as calibrants to connect literature VP values of the PEG compounds to FIGAERO T_{max} values. The calibration curve as defined by equation 1 is not shown on figure 4. It would appear to me that a simple exponential curve does not fit the observed values well. Please include the calibration curve on figure 4, and discuss potential reasons for the deviation from the calibration curve.

Response: this was also raised by reviewer one, please see the detailed response there.

The PEG compounds on figure 3 exhibit different desorption profiles, that is, some are much broader than others. Why?

Response: It is not clear why there are different desorption profiles seen in our data. As already noted in past responses whilst significant concentration variability and perturbed ramp rates might lead to such behaviour, our experiments were well constrained and with proper due diligence as highlighted by referee #1.

How were the PEG compounds introduced? Injected? Individually or together? Same heating ramp rate for each PEG? Are the four thermograms of each PEG of the same amount introduced? Have the authors tried injecting widely ranging amounts of a PEG compound?

Response: The PEG samples were manually syringed on to the filter. These were mostly completed individually but one repeat of 4 and 6 and 5 and 8 were conducted together. This is now clarified in the text.

The concentrations used are now discussed in detail as per the request of reviewer 1. The same heating ramp rate is used, the limitation of this is discussed but as a suggestion to other users it is made clear that the same ramp rate for both the calibrations and measurements should be used in order to reduce the effect of this uncertainty.

"The same cycle was used for the single component measurements for both the GU and UMan instruments. It is however noted that the analysis provided here does not take into account the possibility of a change in ramp rate affecting the T_{max}. It is therefore recommended that the calibration cycles match that of the measurements."

How much does the amount introduced affect the T_{max} value? The amount of OA present can affect the T_{max} values, as reported by many FIGAERO users. This issue can severely affect the applicability of the presented technique, thus the T_{max} dependence on OA loading needs to be addressed carefully. Also, please consider plotting signal versus temperature, not time on figure 3.

From the concentrations used in this study there was no dependence observed in either the PEG calibrations or the chamber experiments. We do however agree that the amount of OA on the filter has the potential to affect the measured T_{max}. This is now clearly discussed in the paper. As per the request of referee 1 the ranges of concentrations used for the calibrations are now included in the paper

“As with any calibration it is recommended to use a comparable amount of calibrant material as would be expected to accumulate during the measurements, as it is noted that the amount of condensed material on the filter can affect the T_{max} .”

We do however reiterate that this paper is presenting this as a method to use and the applicability of the PEG series appropriate calibration of the FIGAERO. We do not suggest that equation one can be utilized widely within the community, although our data may provide a useful reference against which others with the ARI FIGAERO may compare.

The main point of the paper is to use a set of compounds that have been identified as a recommended standard for vapour pressure measurement techniques and apply them to the FIGAERO to overcome previously reported uncertainties (Bilde et al, 2015). While we agree that there are factors that can lead to the variability of the T_{maxes} reported here, such as the concentrations used, we feel our method is robust.

I am particularly concerned with the concept of Tmax for compounds like PEG 4, 5, and 8, all of which show very broad desorption profiles. For these species in particular, the amount introduced, heating ramp rate, etc. can affect Tmax values greatly. Perhaps consider reporting the temperature at which half the mass comes off the filter, as opposed to Tmax.

Response: As described we have thoroughly checked all known parameters that may affect the thermograms reported here and we recognise some of the thermograms are slightly broader than expected, nonetheless as a calibration method for the FIGAERO community to use the authors feel that this is an important step to take for using the FIGAERO in this way.

As used in the Stark et al (2017) paper reporting the temperature at which half the mass comes off the filter looks to show good linearity with the T_{max} . Due to the much greater proportion of the community using T_{max} as well as the lack of correlation with concentration and T_{max} observed here, we have chosen to follow this method for the paper. The following has however been added to the paper to show this as a possible method for other FIGAERO users to employ.

“In this study the T_{max} is reported, however an alternative method, “ T_{50} ”, as described in Stark et al., (2017) uses the temperature at which 50% of the signal is desorbed.”

There is brief mention of alpha-pinene oxidation, but no figures are shown and no results discussed. Please elaborate.

Response: We feel that additional information regarding these experiments is not pertinent to the paper we present here, therefore other than including the total mass measured in this study; additional information is not required in this instance.

line 26 page 4 minor manually extracted?

Response: No change has been made to this;

“Due to the relatively small numbers of thermograms analysed from the UMan FIGAERO-CIMS, the T_{maxes} from the Manchester data were manually extracted.”

line 26 page 2, not Teflon (specific to DuPont product), report specific compound like PFA or PTFE

Response: this has been specified in the text

A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its and its experimental application application to chamber and field studies

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Abstract. The Filter Inlet for Gases and AEROsols (FIGAERO) is an inlet specifically designed to be coupled with the
Aerodyne High Resolution (HR)-Time of flight (ToF)-Chemical ionisation mass spectrometer (CIMS). The FIGAERO-HR-
ToF-CIMS provides simultaneous molecular information relating to both the gas and particle phase samples and has been
25 used to extract vapour pressures of the compounds desorbing from the filter, whilst giving quantitative concentrations in the
particle phase. However, such extraction of vapour pressures of the measured particle phase components requires use of
appropriate, well-defined, reference compounds. Vapour pressures for the homologous series of polyethylene glycols (PEG)
(H-(O-CH₂-CH₂)_n-OH) for n=3 to n=8), covering a range of vapour pressures (VP) (10⁻¹ to 10⁻⁷ Pa) that are
atmospherically relevant have been shown to be reproduced well by a range of different techniques, including Knudsen
30 Effusion Mass Spectrometry (KEMS). This is the first homologous series of compounds for which a number of vapour
pressure measurement techniques have been found to be in agreement, indicating the utility as a calibration standard,
providing an ideal set of benchmark compounds for accurate characterisation of the FIGAERO for extracting vapour
pressure of measured compounds in chambers and the real atmosphere. To demonstrate this, single component and mixture
vapour pressure measurements are made using two FIGAERO-HR-ToF-CIMS instruments based on a new calibration
35 determined from the PEG series. VP values extracted from both instruments agree well with those measured by KEMS and
reported values from literature, validating this approach for extracting VP data from the FIGAERO. This method is then
applied to chamber measurements and the vapour pressures of known products are estimated.

1. Introduction

40 Trace gases and aerosol particles, from anthropogenic and natural sources, are important components of the Earth's climate
system, the components of which vary significantly in terms of properties such as volatility, affecting their impact on air
quality and climate change (Glasius and Goldstein, 2016). There are currently substantial uncertainties in many
physicochemical parameters determining the loading, size, composition and properties of ambient atmospheric aerosol
45 particles, including component vapour pressures (Bilde et al., 2015), that are required to predict their environmental and
human health impacts. This is attributable in large part to the fact that a significant fraction of fine atmospheric aerosol
particles are comprised of organic material (20-90% of particle mass) (Jimenez et al., 2009), containing potentially
thousands of mostly unidentified compounds with properties that are often not well known.

50 This organic aerosol is a major component of the fine particle mass in the atmosphere and is made up of primary organic
aerosol (POA), which is emitted directly from sources such as industry, biomass burning and vehicle emissions but also
secondary organic aerosol formed from the oxidation of gas phase precursors (Robinson et al., 2007). Volatile organic
compounds (VOCs), emitted from both natural and anthropogenic sources, are oxidised through two possible pathways,
fragmentation and functionalization (Donahue et al., 2011). Functionalization can create compounds with a huge range of
55 expected saturation vapour pressures between 0.1 Pa and 10–10 Pa and lower (Jimenez et al., 2009; O'Meara et al., 2014;
Bilde et al., 2015; Tröstl et al., 2016) Functionalization can create multifunctional compounds with molar masses typically
between 150 and 300 g mol⁻¹ and of modest to extremely low volatility with vapour pressures between 0.1 Pa and 10⁻⁷ Pa
(Jimenez et al., 2009; O'Meara et al., 2014; Bilde et al., 2015). The identity, concentrations and properties of such oxidation
60 products are important in order to understand the formation of SOA, but also the general production of oxygenated
compounds partitioning into existing SOA particles that can affect air quality in both outdoor and indoor environments.
Uncertainties in the physicochemical properties of pure components and condensed phase mixtures, as well as absolute

composition, affect our ability to accurately predict this partitioning between the gas and particle phase and the subsequent effects on climate, air quality and fundamentally human health.

The equilibrium vapour pressure of each aerosol constituent is determined, in large part, by its pure component saturation vapour pressure (VP). Saturation VPs of many organic components are poorly known, particularly for the least volatile compounds of interest for atmospheric purposes (Bilde *et al.*, 2015). The importance of this fundamental property is discussed extensively in Bilde *et al.*, (2015) and the sensitivity of predicted mass, composition and particle properties to uncertainties in VP vary according to the complexity of the system being studied, both with regards to the number of compounds used in partitioning and additional processes included in any model (Valorso *et al.*, 2011; O'Meara *et al.* 2014; McVay *et al.* 2016; ~~Ovadnevaite *et al.*, 2017~~). Single-component measurements of vapour pressures by instruments such as the Knudsen Effusion Mass Spectrometry (KEMS), following the methodology of Booth *et al.* (2009) ~~are ongoing~~ have been recently reported (Booth *et al.*, 2012; Bannan *et al.*, 2017) and have been extended to consider vapour pressures in simple multicomponent systems (Booth *et al.*, 2017). Such measurements of are ongoing with the KEMS, focusing on atmospherically relevant compounds. Considerable uncertainty remains when extracting vapour pressure measurements from a single technique, with more work required to resolve the apparent discrepancies between techniques (Bilde *et al.*, 2015). Studies reporting measurements of vapour pressure would benefit from an, at the time unidentified, series of reference standards with volatility ranging across those accessible to the measurement techniques being deployed (Bilde *et al.*, 2015). Following the recommendations of the Bilde *et al.* (2015) study and work within Topping *et al.*, (2018), Krieger *et al.* (2018) identified the homologous series of polyethylene glycols (PEG; $\text{H}-(\text{O}-\text{CH}_2-\text{CH}_2)_n-\text{OH}$) for $n=3$ to $n=8$) as a series of compounds with vapour pressures exhibiting very good agreement (data was consistent with the 95% confidence interval of a linear regression to all measurements) over a wide atmospherically relevant VP range when measured using different experimental methods. This series therefore provides an ideal benchmark for characterising individual VP measurement techniques.

The High Resolution (HR)-Time of flight (ToF)-Chemical ionisation mass spectrometer (CIMS) coupled with the Filter Inlet for Gases and Aerosols (FIGAERO) hereafter referred to as the FIGAERO-CIMS, has the potential to provide compound specific volatility information from ambient aerosol particles (Lopez-Hilfiker *et al.* 2014). The FIGAERO system was first introduced by Lopez-Hilfiker *et al.* (2014) and was subsequently commercialized by Aerodyne Research, Inc. (ARI) to be adaptable to the TOF-CIMS system. The FIGAERO inlet provides molecular determination of gas and particle phase samples. During the gas phase measurement mode, particles from the aerosol sample are collected on a ~~PTFE~~ Teflon filter. After a period of collection, the filter is moved to the inlet of the instrument and dry, heated nitrogen is passed through it to vaporise the particulate for analysis by the TOF-CIMS. The evolution of the MS signals from different compounds change independently as a function of temperature creating a thermogram that is m/z specific. The temperature for which the desorbed signal shows a maximum for each compound, and has been used previously to extract vapour pressure information in laboratory characterisation (Lopez-Hilfiker *et al.*, 2014) and field work studies (Lopez-Hilfiker *et al.* 2016; D'Ambro *et al.*, 2017). A model framework has recently been developed to retrieve volatility and mass transport information from this inlet (Schobesberger *et al.*, 2018). Such online analysis with high temporal resolution has the potential to improve our quantitative and detailed understanding of the diurnal evolution of gas and particle phase composition and based on the use of this inlet to provide VP information, applying the series identified by the Krieger *et al.*, (2018) study for calibrations will be of benefit to the accuracy of future derived measurements of this type.

In this study we will therefore demonstrate the use of this PEG series calibration dataset as a method for extracting quantitative vapour pressures from the FIGAERO inlet. The Figaero system used here is the version produced by Aerodyne Research, Inc. (ARI). Single component measurements made with two separate ARI FIGAERO inlets for compounds of known VP are reported. The application of the FIGAERO to characterise the volatility of species produced in a chamber experiment is then described as a demonstration of the application of this method to a more complex matrix of components.

2. Methodology

2.1 Choice of Reference compounds

The vapour pressure of the Polyethylene glycol (PEG) series, as described in the Krieger *et al.*, (2018) study, were measured by multiple techniques; KEMS (Booth *et al.*, 2009), electrodynamic balance instruments (Zardini *et al.*, 2006; Rovelli *et al.*, 2016) and Tandem Differential Mobility Analyser (TDMA) including a laminar flow tube (Bilde *et al.*, 2003)). The reported vapour pressure of the PEG series demonstrated good agreement between these techniques over a wide range of VPs (spanning five orders of magnitude from about 10^{-1} to 10^{-7} Pa at room temperature). These measurements also compared well to data extrapolated from high temperatures, suggesting that the thermal energy utilised in techniques such as the FIGAERO will not lead to chemical modification of the target molecules. The physical state of the reference compound is important to consider when making VP measurements (Soonsin *et al.*, 2010; Bilde *et al.*, 2015). If the saturation vapour pressure of a compound is measured in the solid state, it needs to be converted to that of the subcooled liquid for use and interpretation within atmospheric models, which can add additional uncertainty through the required conversion. The PEG series therefore act as ideal reference materials as its members are all liquid at the temperatures at which the measurements are routinely performed.

The PEG compounds used in this study show no evidence of degradation with either the age or temperature at which the sample is measured. Measurement of PEG-4 VP by KEMS multiple times over a 6-month period showed no variation beyond measurement uncertainties and data up to temperatures of 450 K reported in the literature are consistent with those measured at room temperature, demonstrating their thermal stability (Krieger *et al.*, 2018). The stability of the PEG compounds allowed samples to be shared between the co-authors of Krieger *et al.*, (2018), ensuring sample conformity.

As saturation vapour pressures of dicarboxylic acids have been determined with a large number of techniques and different instruments over a substantial temperature range, Bilde *et al.* (2015) evaluated the combined data sets providing best estimates with uncertainty ranges for each of the straight-chain dicarboxylic acids. Therefore, these dicarboxylic acids are also used to validate the use of the PEG series as a calibration standard. It should be noted that measurements with the KEMS have suggested that samples of the dicarboxylic acids degrade over long periods of storage (~~approx.~~ \geq 6 months \pm) and can influence the measured vapour pressure. Appropriate storage and quick use of the chemicals, or appropriate purification methods is therefore deemed essential for such measurement studies.

Tetraethylene glycol (PEG-4) (99%) was purchased from Sigma-Aldrich and PEG-5 to 8 were purchased from Polypure AS, Oslo, Norway with purities of 99% or higher and used with no further preparation. All PEG samples were stored in a fridge. Dicarboxylic acids were purchased from Sigma-Aldrich, again with purities of 99% or higher and used with no further preparation. All dicarboxylic acids and samples used were measured within one month of receiving the samples and stored in accordance with the suppliers' recommendations.

2.2 FIGAERO- CIMS

This study utilized two FIGAERO-CIMS, operated by the University of Manchester (UMan) and Gothenburg University (GU) groups. Both FIGAERO systems were manufactured by Aerodyne Research Inc. and employ the ARI/ToFwerk high resolution Time of Flight Chemical Ionisation Mass Spectrometers (TOF-CIMS), similar to that described by Lee *et al.*, (2014). The FIGAERO inlet coupled to a reduced pressure ion molecule reaction (IMR) region, which is in turn coupled to high resolution time of flight mass spectrometer (API-ToF) (Junninen *et al.*, 2010). The ARI FIGAERO inlet used in this work is similar to that described by Lopez-Hilfiker *et al.* (2014). A brief description of the ARI FIGAERO system follows. The UMAN CIMS was operated with iodide as the reagent ion and the GU CIMS was operated with acetate ~~and-or~~ iodide as the reagent ion.

The ARI FIGAERO assembly is shown in ~~F~~Figure 1. The FIGAERO is a two-port inlet, one dedicated to gas sampling (all Teflon) and the second dedicated to aerosol sampling (all metal). The FIGAERO couples both inlets with chemical ionization region of the ToF MS. The FIGAERO operates in two modes, one being ambient air sampling for trace gas analysis with the CIMS, while simultaneously collecting particles on a PTFE filter from a separate inlet. The second mode is the thermal desorption of the collected particles in nitrogen allowing the detection of the desorbed vapours with the CIMS. When in the thermal desorption mode, the exclusively gas phase port to the CIMS is blocked by the moveable tray and the PTFE filter is moved to the exclusive port for thermal desorption. In this position 2 SLM of temperature controlled nitrogen flow is delivered across the filter, desorbing the collected components from the filter. This is known as the Temperature Ramp phase. The evolution of the MS signals from different compounds ~~the filter is exposed to during~~ the Temperature Ramp phase change independently as a function of temperature creating thermograms that ~~are-is~~ m/z specific. T_{max} is ~~defined-measured~~ as the temperature just above the filter, as shown in ~~F~~Figure 2. Two 150W cartridge heaters are used to heat a copper block that connects with a $\frac{1}{4}$ " OD copper tube. The nitrogen desorption gas is heated as flows through this hot copper section which is also nickel plated. The combined length of the copper block and the $\frac{1}{4}$ " copper tube is 16 cm and is set based on thermal modelling to provide maximum heat transfer for the ~ 2 SLPM N_2 desorption gas flow maintained by a programmable mass flow controller. ~~The gas temperature is measured by a 1/16" diameter thermocouple positioned inside and just near the exit of the 1/4" OD copper tube (~5 mm above the PTFE Teflon filter as detailed in Figure 2). The gas temperature is measured by a 1/16" diameter thermocouple positioned inside and just near the exit of the 1/4" OD copper tube (~5 mm above the PTFE Teflon filter).~~ A $\frac{1}{2}$ " OD stainless steel tube 14.6 cm in length is soldered to the copper heater block and provides thermal isolation and mechanical mounting of the heater unit to the FIGAERO assembly.

The temperature at which the desorbed signal for a compound reaches a maximum is used here to extract vapour pressure information. Once the Temperature Ramp phase is complete, under normal operating conditions, the nitrogen is then held at the maximum desorption temperature for a programed period of time to ensure that all of the collected components have been removed from the filter, known as the Temperature Soak phase. After each Ramp and Soak phase the heating is turned off and the unheated nitrogen is then used too cool the filter (Cooling Phase), allowing the filter to return to the starting temperature, before the moveable tray switches back to trace gas analysis and filter collection of particulate matter.

The UMan TOF-CIMS has been described in detail by Priestley *et al.*, (2018a; 2018b). The UMan FIGAERO-CIMS was exclusively run with iodide as the reagent ion during this study, as described in Reyes Villegas *et al.*, (2018) and it was this system that measured the ~~peg-PEG~~ series only. The GU CIMS (Faxon *et al.*, 2018; Le Breton *et al.*, 2017; Le Breton *et al.*, 2018) hardware is identical to that of the UMan CIMS although tuning of the ion optics and flows differ to optimize the signal to noise ratio and total ion counts. Results from both acetate and iodide reagent ions from the GU FIGAERO-CIMS are presented here.

Prior to each sample measurement being made using both the GU and UMan FIGAERO-CIMS instruments, background measurements were obtained. First, a new filter was placed in the FIGAERO and the temperature was ramped to 200°C for 10 minutes to ensure the filter was clean and then cooled. A ramp, soak and cool cycle matching that of the subsequent sample was then completed to obtain the background. During the PEG series measurements the filter was ramped to 200°C (temperature above the filter) over a period of 20 minutes (at a rate of 8.75°C min⁻¹), held at 200°C for 10 minutes and finally allowed to cool back to room temperature for a period of 5 minutes. The same cycle was used for the single component measurements for both the GU and UMan instruments. It is however noted that the analysis provided here does not take into account the possibility of a change in ramp rate affecting the T_{max}. It is therefore recommended that the calibration cycles match that of the measurements. Temperature cycles and gas flows were controlled using the ARI EyeOn™ control system.

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Using the UMan FIGAERO, measurement of the PEG series were performed by first using a blank filter as a background then on a new filter depositing the PEG sample on the Zefluor® PTFE membrane filter (2 micron pore size) for each desorption, cleaning and then re-running with the next PEG sample. Four desorptions of each PEG were performed by depositing 0.1 µl of two different concentrations (two repeats of each), of 200 µg cm⁻³ and 2000 µg cm⁻³, with a mean of the 4 desorptions being reported as the T_{max}. No linear dependence of T_{max} with concentration was observed across this concentration range. As with any calibration it is recommended to use a comparable amount of calibrant material as would be expected to accumulate during the measurements, as it is noted that the amount of condensed material on the filter can affect the T_{max}. A range of calibration concentrations larger than that reported in this study is suggested for future studies and the small range is noted here as a limitation of this study. PEG calibrations were generally conducted individually and were manually syringed on to the filter. The reported T_{max} value for the one of highest concentration runs for PEG 4 and PEG 6 as well as PEG 5 and PEG 8 were mixed in two separate experiments. The conditions were designed to ensure that the T_{max} of the PEG series was not mixture dependent, although a more detailed study is required. This was completed on both singularly and under mixed (PEG 4 to 6 and 5 to 8) conditions to ensure that the T_{max} of the PEG series was not mixture dependent. For the single component measurements other than the PEG series, a known mass of the species to be calibrated is added to a solvent (methanol or deionized water) to create a known concentration in the solvent and then 0.1 µl of it is placed onto the Zefluor® PTFE membrane filter using a syringe injector.

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The FIGAERO-CIMS instrument analysis software (ARI Tofware version 2.5.11) was utilized to attain high resolution, 1Hz, time series of the compounds presented here. For the UMan CIMS, mass-to-charge calibration was performed for 5 known masses; I⁻, I⁻.H₂O, I⁻.HCOOH, I₂⁻, I₃⁻, covering a mass range of 127 to 381 m/z. The mass-to-charge calibration was fitted to a 3rd order polynomial and was accurate to within 2 ppm; ensuring peak identification was accurate below 3 ppm. The PEGs were detected as adducts in the UMan experiments i.e. I.(H-(O-CH₂-CH₂)_n-OH), where n=4 to 8.

Due to the relatively small numbers of thermograms analysed from the UMan FIGAERO-CIMS, the T_{maxes} from the Manchester data were manually extracted. The average (mean) of the maximum 3 values in the thermogram is averaged used (mean) to extract the T_{max} values reported here. For the GU FIGAERO data a more automated FIGAERO thermograms were evaluated with the GUFIT (Gothenburg University Fitting for Thermograms) procedure, method was used. Python packages, NumPy (v 1.11.3), SciPy library (v 0.18.1) and pandas (v 0.19.2) were utilized for peak finding and curve fitting algorithm. An exponentially modified Gaussian (Foley and Dorsey, 1984) was used as the peak shape function and the desorption temperature values of the peaks as initial guesses for curve fitting. The single thermogram attained initially has a background fitted to the peak to reduce instrumental noise error on the desorption profile integration and then a mathematical fit is applied which is utilised to attribute either a single or multiple desorption profile in which the T_{max} can be retrieved which is described in detail in the supplementary material. In this study only the T_{max} is reported, however an alternative method, "T50", as described in Stark et al., (2017) uses the temperature at which 50% of the signal is desorbed, could also have been employed here.

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2.3 Chamber Experiments

In addition to the PEG VP calibrations, we also performed FIGAERO measurements of secondary organic aerosols generated in the Manchester Photochemical Aerosol Chamber and vapor pressures of several organic acids (mass accuracy all <2 ppm) from measurements made in these experiments are reported here. Briefly, the chamber consists of an 18 m³ Teflon bag illuminated by a bank of halogen lamps and two 6 kW Xenon arc lamps simulating the solar spectrum (further details can be found in Alfarra et al., (2012, 2013)). The air charge in the bag was dried and filtered for gaseous impurities and particles, prior to humidification with high purity de-ionised water. The biogenic SOA precursor α-pinene was injected into the chamber with an initial mixing ratio of 125 ppb. NO_x was added with initial mixing ratios of 30 ppb. The relative humidity was 40% and the temperature was 25°C.

Gas phase measurements were made from the chamber through a 0.75 m long PTFE 6.5 mm OD unheated inlet drawn at 2.2 SLM. Particles were collected through a 1.0 m stainless steel 6.2 mm OD inlet at a flow rate of 2 SLM. The same procedure for obtaining the filter background and the same thermal desorption cycle as used in the UMan FIGAERO-CIMS PEG

experiments were utilised for the chamber experiments. First, a new filter was placed in the FIGAERO and the temperature was ramped to 200°C for 10 minutes to ensure the filter was clean and then cooled. A ramp, soak and cool cycle matching that of the subsequent sample was then completed to obtain the filter background. In addition, and after the filter background, a chamber background was then taken daily that involved a 45 minute filter collection of air from the chamber with no VOC added and with no detectable particles in the chamber and subsequent desorption. The chamber experiments were performed using a 45 minute trace gas analysis and collection on to the PTFE filter.

2.3.4 FIGAERO-CIMS for Vapour Pressure Measurements

Previous VP measurements have revealed discrepancies in vapour pressures between instruments that differ between compounds depending on the functional groups they contain. In such previous studies it has not proven straightforward to attribute low or high biases to a particular technique, as shown in the Huisman *et al.*, (2013) study. In the following analysis it is assumed there are no functional group or compound specific dependencies applicable to the FIGAERO, for either the PEG, single components or unknown compound analysis. This work also makes the necessary assumption that this filter-based measurement in an uncharacterized mixed matrix yields [single component](#) sub-cooled liquid VPs.

The methodology for retrieving vapour pressures we present in this paper may be subject to some biases when applied to complex chemical systems and this needs to be borne in mind when interpreting results. When measuring thermograms of multi-component systems collected on the FIGAERO, the desorption profiles can exhibit double and/or non-Gaussian peak shapes, often explained by decomposition of higher molecular weight compounds. The thermal decomposition of higher molecular weight compounds can certainly generate errors in the FIGAERO-CIMS T_{\max} measurements. This is because any lower molecular weight fragments generated by decomposition will exhibit T_{\max} values representative of the T_{\max} of the higher molecular weight molecule from which the fragment was generated. [There also may be fragmentation of weak bonds in the particulate phase, also giving an unrepresentative \$T_{\max}\$ and desorption profile. A detailed discussion of such factors is given in Stark *et al.*, \(2017\).](#) Furthermore, inherent to [mass spectrometry and CIMS](#), whilst the molecular composition can be determined, the molecular structure is not known and assumptions have to be made based on likely functional groups present in the system (chamber or environment) that is being measured. Recent studies (Booth *et al.*, 2012; Bannan *et al.*, 2017; Dang *et al.*, 2018) have shown how subtle differences in molecular structure have a significant impact upon vapour pressure. Booth *et al.*, (2012), for example, measured the role of ortho, meta, para isomerism in measured solid state and derived sub-cooled liquid vapour pressures of substituted benzoic acids and observed variations of up to 3 order magnitude as a function of this isomerism. Such isomers cannot be differentiated with the CIMS and therefore the assignment of measured T_{\max} of compounds with this functional group positioning effect could be dubious and provide broadening or additional peaks, thus affecting the definition of the T_{\max} and our methodology presented here.

2.4 Chamber Experiments

~~In addition to the PEG-VP calibrations, we also performed FIGAERO measurements of secondary organic aerosols generated in the Manchester Photochemical Aerosol Chamber and vapor pressures of several organic acids are reported here. Briefly, the chamber consists of an 18 m³ Teflon bag illuminated by a bank of halogen lamps and two 6 kW Xenon arc lamps simulating the solar spectrum (further details can be found in Alfara *et al.*, (2012, 2013). The air charge in the bag was dried and filtered for gaseous impurities and particles, prior to humidification with high purity de-ionised water. The biogenic SOA precursor α pinene was injected into the chamber with an initial mixing ratio of 125 ppb. NO_x was added with initial mixing ratios of 30 ppb. The relative humidity was 40% and the temperature was 25°C.~~

~~Gas phase measurements were made from the chamber through a 0.75 m long PTFE 6.5 mm OD unheated inlet drawn at 2.2 SLM. Particles were collected through a 1.0 m stainless steel 6.2 mm OD inlet at a flow rate of 2 SLM. The same procedure for obtaining the filter background and the same thermal desorption cycle as used in the UMan FIGAERO-CIMS-PEG experiments were utilised for the chamber experiments. In addition a chamber blank was then taken under the same conditions as the sample run on that day, where a 45 minute collection on the filter and subsequent desorption was completed in a chamber with no VOC added and with no detectable particles in the chamber. The chamber experiments were performed using a 45 minute trace gas analysis and collection on to the PTFE filter.~~

3. Results

3.1 The relationship between VP and T_{\max}

Thermograms are shown in Figure 3 for the PEG samples as measured by the UMan FIGAERO-CIMS, from which the T_{\max} es are retrieved in a process described above. T_{\max} values for the PEG compounds are summarized in Table 1 where we also compare our determinations against literature VP measurements reported VPs at 298 K for the PEG series (Krieger *et al.*, 2018), and illustrated in [Figure 4](#). The vapour pressure range of the PEG series covers [and extends](#), an atmospherically relevant range between 1 and 10^{7.4} Pa, where compounds with $P_{298K} > 1$ Pa exist entirely in the gas phase under atmospherically reasonable conditions and compounds with $P_{298K} < 10^{-4}$ Pa will exist largely in the particle phase (Valorso *et*

al., 2011). This range of compounds allows characterisation of the FIGAERO across the range of volatilities that are most important throughout the lower atmosphere.

A single exponential fit to the data on the VP at 298 K derived from the PEG series and extracted T_{\max} can provide a relationship between T_{\max} and VP:

$$VP \text{ (Pa)} = 0.2612 \exp^{-0.071 T_{\max}}, \text{ with } T_{\max} \text{ in } (^{\circ}\text{C}). \quad (1)$$

3.2 Evaluating the VP calibration for FIGAERO using single compounds with known VP

The PEG VP calibration can be used to derive the VP of other compounds measured by the FIGAERO ToF-CIMS by extracting the T_{\max} of compounds and applying equation 1 to the measured value. By choosing a range of compounds with known and characterized VP the calibration can be evaluated and may then be utilized for compounds of unknown VP that can be measured with the CIMS.

By way of validation Table 2 and Figure 5 show laboratory single component measurements of T_{\max} for a variety of carboxylic acid species, alongside both literature values of their vapour pressure and their calculated vapour pressures using the PEG calibration curve. Whilst these measurements come from both the UMan and GU FIGAERO-CIMS, the PEG series was not measured by the GU FIGAERO-CIMS. Therefore the same calibration function, derived from the UMan CIMS, is utilised for other instruments. Table 3 and Figure 6 report extracted T_{\max} and calculated VPs from a chamber experiment in the Manchester Aerosol Photochemical Chamber using the UMan FIGAERO-CIMS. Where possible the recommended VP values from the Bilde *et al.*, (2015) study are used for comparison, as these are the best available literature values available other than the PEG series.

Using the PEG series calibration for single component measurements it is clear from Table 2 that there is a good agreement between the FIGAERO and literature vapour pressures. The measurements from the chamber also show a good agreement, with an average overestimation of 67%, which is still well within the reported error of instruments such as the KEMS in the subcooled liquid state (Booth *et al.*, 2012). Figures 5 and 6 show that for the compounds presented by Bilde *et al.*, (2015), as well as selected others, the GU and UMan T_{\max} extracted VPs agree very well with the literature. This shows that the PEG series calibration could potentially be applied for different instruments and different reagent ions, depending of course on the configuration and generation of FIGAERO that is being used. Nevertheless, calibration of individual FIGAERO inlets is highly recommended as small changes in the position of the thermocouple, contact time with the heater and nitrogen, nitrogen flow rate, surface area of the filter among other factors can affect thermograms.

4. Discussion and Outlook

We present here the calibration of two FIGAERO inlets coupled to the ToF-CIMS for extracting volatility information from single component and chamber measurements. Recent comparison of ~~atmospheric component~~ vapour pressure measurement techniques (Krieger *et al.*, 2018) has identified the PEG series as a group of compounds that can be trusted as reference compounds for a range of measurement methods that across ~~the full~~ wide range of tropospheric representative vapour pressures. This paper shows that this series can be used to calibrate the vapour pressure of single components using the FIGAERO inlet coupled to ToF-CIMS. We have evaluated the derived vapour pressures against a wider range of atmospherically relevant single compounds and compounds identified in chamber oxidation experiments that have a known vapour pressure and demonstrate consistency with other VP techniques. This offers a pathway to determining VPs from FIGAERO-ToF-CIMS for the many atmospheric compounds that are not yet characterised.

We do note that the FIGAERO is not interference free, mixtures affecting single component VPs and state differences in mixed component systems will affect retrieved VPs especially when organic aerosol concentrations are high. Despite the seemingly good agreement with the UMan and GU FIGAERO for the measurements reported here, it is necessary to independently calibrate each FIGAERO inlet, especially when using a generation of FIGAERO different to the commercially available inlet. The authors believe that such single component measurements of reference compounds, most accurately and confidently using the PEG series, are essential for understanding the extracted information from the FIGAERO, and other VP measurement techniques, in order to better understand the atmospheric implications of such measurements.

The stability of the PEGs allowed sharing of samples to ensure the same quality between the institutions as those that participated in the Krieger *et al.*, (2018) study. Samples should be stored, handled and measured on the same time scale to reduce as much as possible the chance of contamination. We propose that the same procedure could be undertaken to run an inter-comparison between different FIGAERO inlets.

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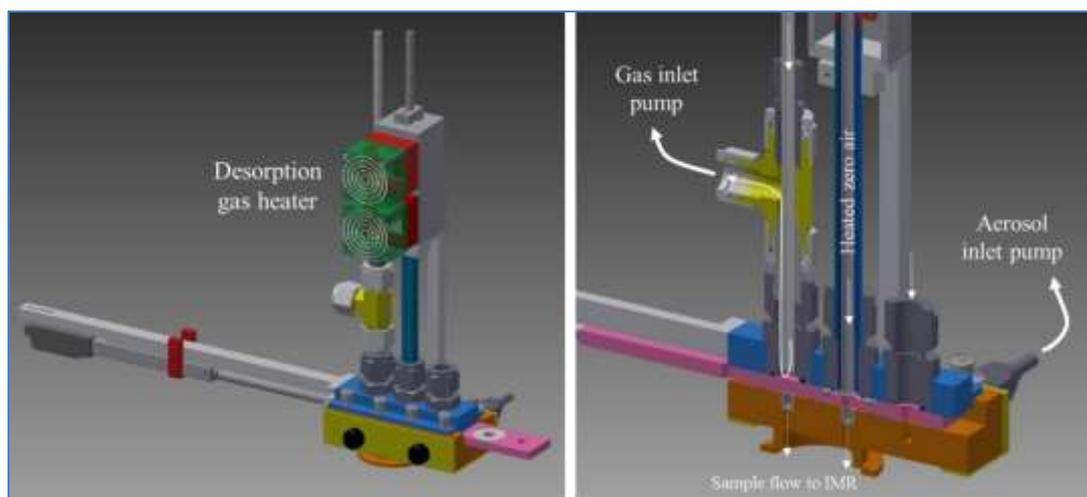


Figure 1: Drawing of the ARI FIGAERO assembly. Panel on left shows full assembly with mechanical actuator that controls gas sampling/aerosol collection or aerosol desorption operating modes. Panel on right is a cross-sectional view that show flows for both gas and particle sampling mode and the two apertures that connect with the IMR. In this view the FIGAERO slide is positioned in the aerosol desorption mode and the gas sample flow into the IMR is closed.

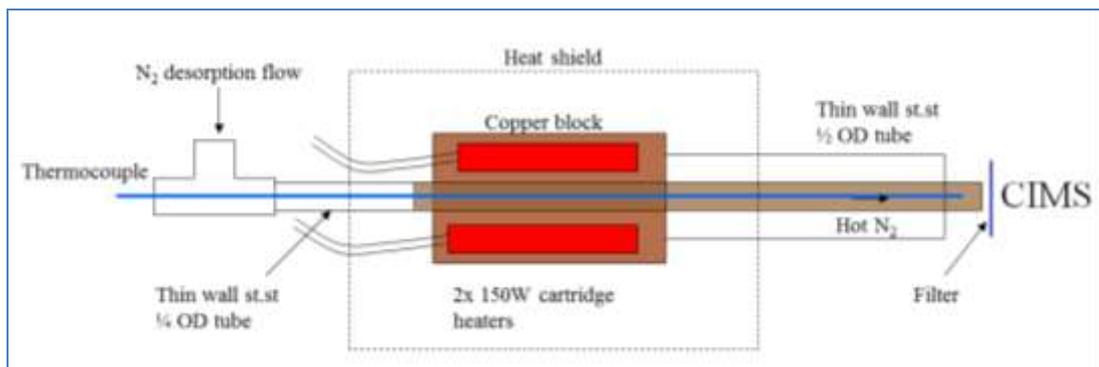


Figure 2: internal schematic of the FIGAERO desorption gas heater unit. Temperature above the filter is measured at the end point of the heated tube by the long thermocouple running through the inlet, shown here in blue.

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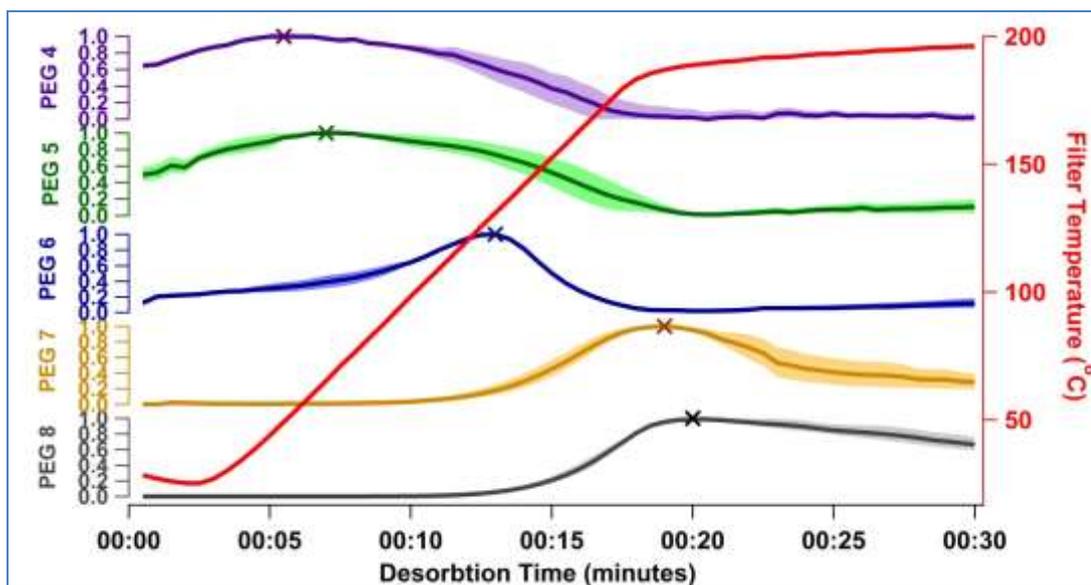


Figure 3: Thermograms from the PEG series as detected by the FIGAERO-CIMS employing Iodide adduct ionization, all product ion intensities are normalised to 1. Thick coloured lines show the mean of the thermograms and the associated shaded areas show the standard deviation of the 4 thermograms. Crosses show the extracted T_{max} . Red line shows the temperature just above the filter.

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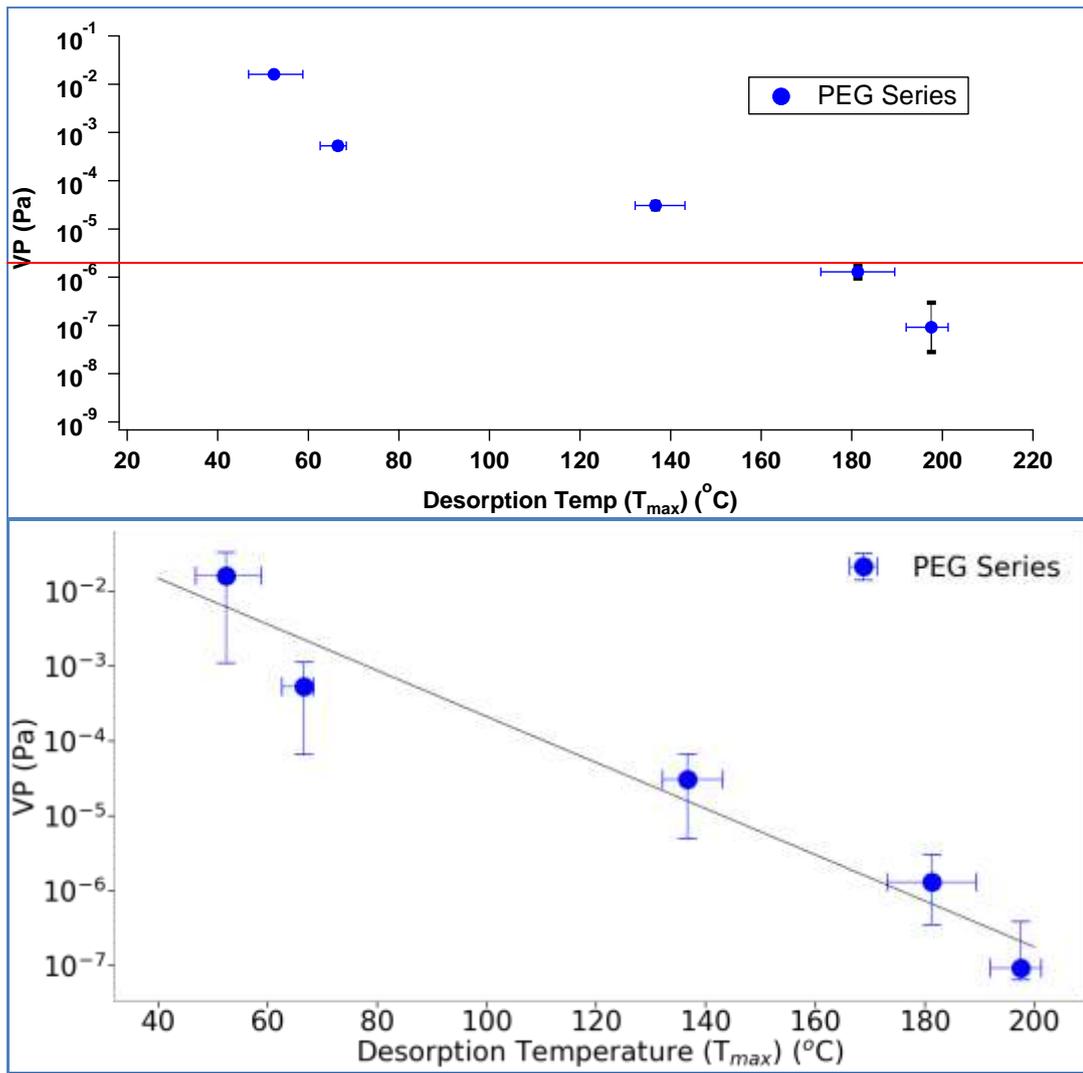


Figure 4: Reported vapour pressure measurements of the PEG series (4-8) and associated T_{max} values extracted from the UMan FIGAERO-CIMS. Errors on the y-axis are those reported in the Kreiger et al., (2018) study. Errors in the T_{max} (x-axis) are the maximum variation seen within the 4 thermograms from which the mean value was derived.

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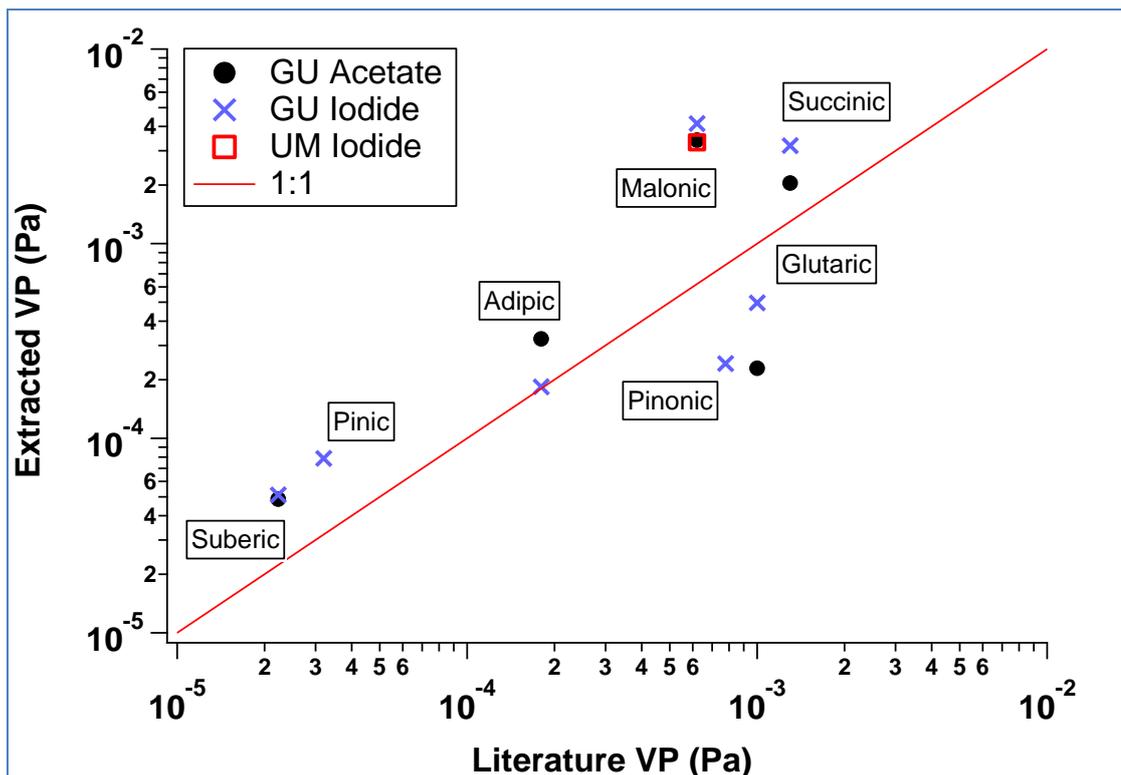


Figure 5: Extracted VP from the UMan and GU FIGAERO-CIMS, plotted against reported subcooled saturation vapour pressures from the literature, through utilization of the PEG calibration. These measurements are made using single compounds from the UMan and GU FIGAERO-CIMS (see Table 3).

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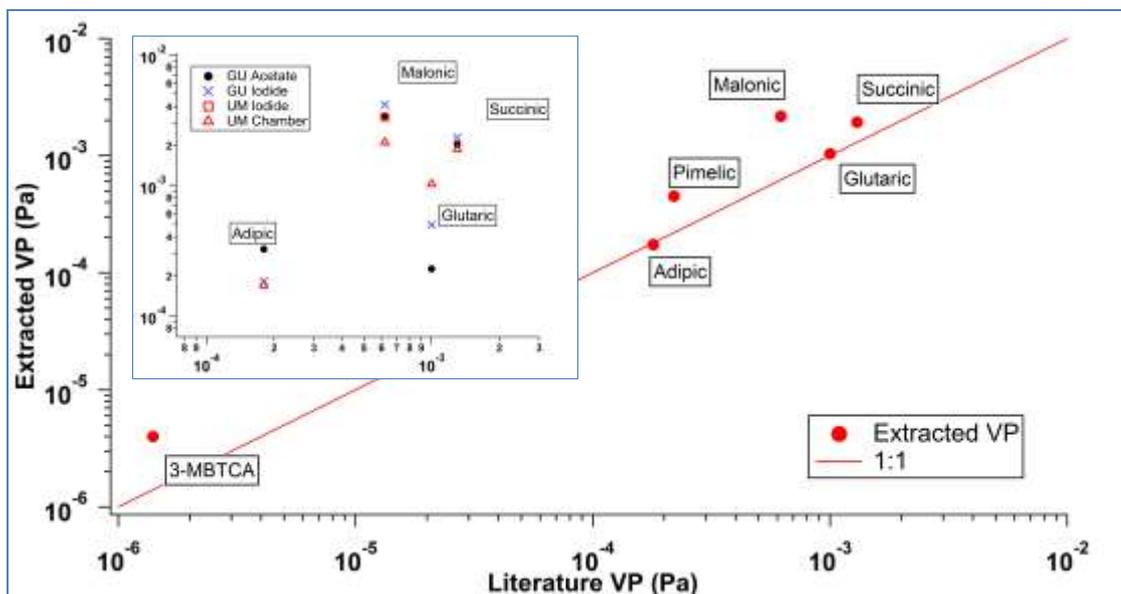


Figure 6: Extracted VP from the UMan FIGAERO plotted against reported VPs from the literature. These measurements are made using the UMan instrument from the Manchester SOA chamber experiments (see Table 3). Direct comparisons are made for adipic, glutaric, malonic and succinic acids, which were measured in both the single component and chamber study, shown on the inset panel, axis are as described in the main figure. **Total mass concentrations in the chamber ranged from 0-60 $\mu\text{g m}^{-3}$ throughout the complete experiment.**

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Table 1: Reported vapour pressure measurements of the PEG series (4-8) at 298.15 K (Krieger *et al.*, 2018) and associated T_{\max} values extracted from the UMan FIGAERO- CIMS. All T_{\max} values are an average of 4 individual thermograms for each PEG sample. Errors in the T_{\max} are the maximum variation seen within the 4 thermograms.

PEG	VP (Pa)	T_{\max} ($^{\circ}$ C)
4	$1.69 \begin{smallmatrix} +0.11 \\ -0.10 \end{smallmatrix} \times 10^{-2}$	$52.4 \begin{smallmatrix} +6.4 \\ -5.6 \end{smallmatrix}$
5	$5.29 \begin{smallmatrix} +0.75 \\ -0.65 \end{smallmatrix} \times 10^{-4}$	$66.5 \begin{smallmatrix} +1.8 \\ -3.9 \end{smallmatrix}$
6	$3.05 \begin{smallmatrix} +0.58 \\ -0.49 \end{smallmatrix} \times 10^{-5}$	$136.6 \begin{smallmatrix} +6.5 \\ -4.5 \end{smallmatrix}$
7	$1.29 \begin{smallmatrix} +0.48 \\ -0.35 \end{smallmatrix} \times 10^{-6}$	$181.3 \begin{smallmatrix} +8.1 \\ -8.1 \end{smallmatrix}$
8	$9.20 \begin{smallmatrix} +20.4 \\ -6.4 \end{smallmatrix} \times 10^{-8}$	$197.5 \begin{smallmatrix} +3.7 \\ -5.6 \end{smallmatrix}$

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Table 2: Extracted T_{\max} values and calculated VPs through utilization of the PEG calibration compared against literature data of subcooled saturation vapour pressures. A single component measurement is defined as a single calibration compound being placed on the filter and desorbed as per the description in the methods.

Compound	Detected As	T_{\max} ($^{\circ}$ C)	Reagent Ion and Instrument	FIGAERO VP (Pa)	Literature VP (Pa)	Source
Malonic	I.C ₃ H ₄ O ₄ -	61.5	UMan Iodide	3.32×10^{-3}	6.20×10^{-4}	Bilde <i>et al.</i> , 2015
	I.C ₃ H ₄ O ₄ -	58.4	GU Iodine	4.13×10^{-3}	6.20×10^{-4}	Bilde <i>et al.</i> , 2015
	C ₃ H ₃ O ₄ -	61.2	GU Acetate	3.39×10^{-3}	6.20×10^{-4}	Bilde <i>et al.</i> , 2015
Succinic	I.C ₄ H ₆ O ₄ -	62.1	GU Iodine	3.18×10^{-3}	1.30×10^{-3}	Bilde <i>et al.</i> , 2015
	C ₄ H ₅ O ₄ -	68.3	GU Acetate	2.05×10^{-3}	1.30×10^{-3}	Bilde <i>et al.</i> , 2015
Glutaric	I.C ₅ H ₈ O ₄ -	88.3	GU Iodine	4.95×10^{-4}	1.00×10^{-3}	Bilde <i>et al.</i> , 2015
	C ₅ H ₇ O ₄ -	99.2	GU Acetate	2.28×10^{-4}	1.00×10^{-3}	Bilde <i>et al.</i> , 2015
Adipic	I.C ₆ H ₁₀ O ₄ -	102.3	GU Iodine	1.83×10^{-4}	1.80×10^{-4}	Bilde <i>et al.</i> , 2015
	C ₆ H ₉ O ₄ -	94.3	GU Acetate	3.23×10^{-4}	1.80×10^{-4}	Bilde <i>et al.</i> , 2015
Suberic	I.C ₈ H ₁₄ O ₄ -	120.3	GU Iodine	5.10×10^{-5}	2.23×10^{-5}	Booth <i>et al.</i> , 2011
	C ₈ H ₁₃ O ₄ -	121	GU Acetate	4.85×10^{-5}	2.23×10^{-5}	Booth <i>et al.</i> , 2011
Pinonic	I.C ₁₀ H ₁₆ O ₃ -	98.4	GU Iodine	2.41×10^{-4}	7.78×10^{-4}	Booth <i>et al.</i> , 2011
Pinic	I.C ₉ H ₁₄ O ₄ -	114.2	GU Iodine	7.86×10^{-5}	3.20×10^{-5}	Bilde and Pandis 2001

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Table 3: Extracted T_{\max} values and VP at 298k from chamber SOA experiments as measured by the UMan Iodide FIGAERO-CIMS. T_{\max} are an average measured over the 7 desorptions (not including background) from the chamber experiment. **Errors in the T_{\max} are the maximum variation seen within the 7 thermograms. Total mass concentrations in the chamber ranged from 0-60 μ g m^{-3} throughout the complete experiment.**

Compound	Detected As	T_{\max} ($^{\circ}$ C)	FIGAERO VP (Pa)	Comparison VP (Pa)	Source
Malonic	I.C ₃ H ₄ O ₄ -	$67.5 \begin{smallmatrix} +2.61 \\ -1.98 \end{smallmatrix}$	2.17×10^{-3}	6.20×10^{-4}	Bilde <i>et al.</i> , 2015
Succinic	I.C ₄ H ₆ O ₄ -	$69.1 \begin{smallmatrix} +2.97 \\ -4.63 \end{smallmatrix}$	1.93×10^{-3}	1.30×10^{-3}	Bilde <i>et al.</i> , 2015
Glutaric	I.C ₅ H ₈ O ₄ -	$77.8 \begin{smallmatrix} +3.0 \\ -2.9 \end{smallmatrix}$	1.04×10^{-3}	1.00×10^{-3}	Bilde <i>et al.</i> , 2015
Adipic	I.C ₆ H ₁₀ O ₄ -	$103.0 \begin{smallmatrix} +2.60 \\ -1.80 \end{smallmatrix}$	1.74×10^{-4}	1.80×10^{-4}	Bilde <i>et al.</i> , 2015
Pinelic Acid	I.C ₇ H ₁₂ O ₄ -	$89.6 \begin{smallmatrix} +2.35 \\ -2.75 \end{smallmatrix}$	4.51×10^{-4}	2.20×10^{-4}	Bilde <i>et al.</i> , 2015
3-MBTCA	I.C ₈ H ₁₂ O ₆ -	$156.2 \begin{smallmatrix} +2.07 \\ -3.23 \end{smallmatrix}$	3.99×10^{-6}	1.50×10^{-6}	Lienhard <i>et al.</i> , 2015

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A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its application to chamber and field studies

We thank the reviewers for their time evaluating this manuscript and their positive comments relating to this work. The corrections and additions made as a result of these comments have greatly improved the consistency and focus of this work. The response to each point immediately follows each comment and is coloured red.

Anonymous Referee #1

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.

Detailed comments

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.)

Response: The paper title has been changed to: "A method for extracting calibrated volatility information from the FIGAERO-HR-ToF-CIMS and its experimental application"

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 were blank measurements treated?

Response: for the calibration there was no background signal in each thermogram which needed to be analysed. A more detailed background procedure for the chamber experiments is now also included. However, given that quantitative concentration data is not reported, only the behaviour of the desorption profiles, there was no need for subtracting backgrounds from the data reported here.

"First, a new filter was placed in the FIGAERO and the temperature was ramped to 200°C for 10 minutes to ensure the filter was clean and then cooled. A ramp, soak and cool cycle matching that of the subsequent sample was then completed to obtain the filter background. In addition, and after the filter background, a chamber background was then taken daily that involved a 45 minute filter collection of air from the chamber with no VOC added and with no detectable particles in the chamber and subsequent desorption."

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.

Response: The filter used for the blank desorption was used for the following PEG experiment and this has been now better explained in the text. Sections 2.3 and 2.4 have now been switched for better flow of the experimental procedures.

5 *“Prior to each sample measurement being made using both the GU and UMan FIGAERO-CIMS instruments, background measurements were obtained. First, a new filter was placed in the FIGAERO and the temperature was ramped to 200°C for 10 minutes to ensure the filter was clean and then cooled. A ramp, soak and cool cycle matching that of the subsequent sample was then completed to obtain the background. During the PEG series*
10 *measurements the filter was ramped to 200°C (temperature above the filter) over a period of 20 minutes (at a rate of 8.75°C min⁻¹), held at 200°C for 10 minutes and finally allowed to cool back to room temperature for a period of 5 minutes. The same cycle was used for the single component measurements for both the GU and UMan instruments. It is however noted that the analysis provided here does not take into account the possibility of a change in ramp rate affecting the T_{max}. It is therefore recommended that the calibration cycles match that of the measurements. Temperature cycles and gas flows were controlled using the ARI EyeOn™ control system.”*

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.

Response: That is correct – the sentence has been rewritten as;

15 *“Functionalization can create compounds with a huge range of expected saturation vapour pressures between 0.1 Pa and 10⁻¹⁰ Pa and lower (Jimenez et al., 2009; O’Meara et al., 2014; Bilde et al., 2015, Tröstl et al., 2016).”*

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

Response: as detailed in the text it relates to inside the copper tube, however to be clearer a link to Figure 2 is added where the position of the thermocouple in question is illustrated

20 *“The gas temperature is measured by a 1/16” diameter thermocouple positioned inside and just near the exit of the ¼” OD copper tube (~5 mm above the PTFE Teflon filter as detailed in Figure 2).”*

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
25 consistent with 300 °C. I assume the equivalent heating rate for standard desorptions was (300-25)/10 = 27.5 °C?

Response: the notation was here to show that some desorptions during the experiments were run to 200°C and others to 300°C, but we agree that this is not clear. The hotter filter temperature and longer desorption times were used, as described in the text, to enable resolution of multiple peak desorptions and calculation of more
30 accurate T_{max} values, but as all the results presented in this study are based on the measurements up to 200°C, references to the longer desorption and hotter temperatures have been removed as we agree that at 300°C the filters would likely not be thermally stable.

The position of the temperature that is measured is now also clarified in the text

35 *“During the PEG series measurements the filter was ramped to 200°C (temperature above the filter) over a period of 20 minutes (at a rate of 8.75°C min⁻¹), held at 200°C for 10 minutes and finally allowed to cool back to room temperature for a period of 5 minutes.”*

Maybe best if the authors could include that default heating rate, and clarify the issue regarding 200 vs. 300 °C.

Response: agreed. This has now been included.

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.

Response: A substantially expanded and improved description of the details of this method has now been included in the supplementary information for this paper.

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.

Response: the total mass and concentrations of PEG used in this study are now discussed in the following text:

“Four desorptions of each PEG were performed by depositing 0.1 μl of two different concentrations (two repeats of each), of 200 $\mu\text{g cm}^{-3}$ and 2000 $\mu\text{g cm}^{-3}$, with a mean of the 4 desorptions being reported as the T_{max} . No linear dependence of T_{max} with concentration was observed across this concentration range. As with any calibration it is recommended to use a comparable amount of calibrant material as would be expected to accumulate during the measurements, as it is noted that the amount of condensed material on the filter can affect the T_{max} . A range of calibration concentrations larger than that reported in this study is suggested for future studies and the small range is noted here as a limitation of this study. PEG calibrations were generally conducted individually and were manually syringed on to the filter. The reported T_{max} value for the one of highest concentration runs for PEG 4 and PEG 6 as well as PEG 5 and PEG 8 were mixed in two separate experiments. The conditions were designed to ensure that the T_{max} of the PEG series was not mixture dependent, although a more detailed study is required.”

And please plot that fit (Eq. 1) also in Fig. 4.

Response: this has now been added.

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?

Response: We have thoroughly checked all known parameters that may affect the thermograms reported here and whilst we recognise there is rather more variability than may be typical for FIGAERO calibrations we are unsure of the reason. In general, varying concentrations and ramp rates might potentially lead to varying desorption profiles; although in this study we did not perturb ramp rates and, with the concentrations used here we see no direct evidence of this. Given the variability between the past reported responses to VP and Tmax, as reported in Stark et al., (2017) the importance of calibrating individual instruments is reiterated, as many effects noted above can affect the thermograms.

Section 3.2: As commented above regarding section 3.1, please add information about the deposits in those experiment, e.g. in Table 2.

Response: As above, this has now been addressed.

And are the Tmax from single measurements or an average over several repetitions?

Response: The Tmax is a mean over 4 repetitions. This is now stated in the text in section 3.2 where the concentrations of each desorption are now also noted.

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).

The variability for the T_{max} during this experiment is now reported in table 3 as requested below. We see no relationship between the T_{max} and the total mass measured in the chamber, but we agree that this may be an important factor to consider, and is now discussed as below.

5 *“As with any calibration it is recommended to use a comparable amount of calibrant material as would be expected to accumulate during the measurements, as it is noted that the amount of condensed material on the filter can affect the T_{max} . A range of calibration concentrations larger than that reported in this study is suggested for future studies and the small range is noted here as a limitation of this study.”*

The range of total mass observed in the chamber during this measurement period to show that this has been considered in the caption of Figure 6.

10 It could also be interesting to know about the variability in observed T_{max} , as the listed values are the mean of 7 measurements.

Response: the maximum observed variability in the T_{max} from each of the 7 thermograms is now included in table 3.

15 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.

As we have already stated in the paper;

25 *“This work also makes the necessary assumption that this filter-based measurement in an uncharacterized mixed matrix yields single component sub-cooled liquid VPs.”*

30 And therefore the FIGAERO does not produce a mole fraction scaled vapour pressure. We assume that all components, even if they were originally associated with an aqueous solution when in the aerosol, will have precipitated out of solution according to their solubility as the water is driven off and then evaporate as “pure” components. Each compound therefore exhibits their pure component vapour pressure and it will not depend on their mole (or mass) fractions.

35 The ARI FIGAERO inlet used in this work is similar to that described by Lopez-Hilfiker et al. (2014), but not identical and differences in the position of the thermocouple position, flows and general configuration of the FIGAEROs will have implications for the reported T_{max} values from each instrument. This discussion is however outside the scope of the paper as we are presenting a method of calibration for each user and not the direct translation of results.

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.

Response: Agreed, this paper is now referenced several times throughout the revised manuscript.

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.)

Response: That is correct; this has been corrected in the text.

5 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.

Response: There was a mistake in that sentence, yes. This has been corrected with an amendment to show that this calibration does not cover the full volatility range of atmospherically relevant organics, but a very significant part of it. Amended to:

10 *“Recent comparison of vapour pressure measurement techniques (Krieger et al., 2018) has identified the PEG series as a group of compounds that can be trusted as reference compounds for a range of measurement methods that across a wide range of tropospherically representative vapour pressures.”*

Minor/technical comments

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

p. 2, l. 28: changes. Same in p. 3, l. 37-38, or maybe I am misreading these sentences. Response: change is the correct use here.

p. 2, l. 30: "and" too much? Response: this has been left as is.

p. 2, l. 35: "," too much Response: this has been left as is.

20 p. 3, l. 26: I assume the GU CIMS was operated with either acetate or iodide reagent ions? Response: this is correct and has been clarified in the text.

“GU CIMS was operated with acetate or iodide as the reagent ion.”

25 p. 3, l. 38: Definition of T_{max} is inconsistent with its definition before (and again at p. 3, l. 48). Probably wrong use of "defined". Response: yes, defined is the wrong use here. This has been change to "measured" in reference to the position that the T_{max} is measured.

p. 4, l., 41: I find the sentence hard to follow Response: this sentence has now been changed slightly.

p. 4, l. 64: odd amount of brackets Response: this has been corrected.

p. 5, l. 20: unclear meaning of "extend" Response: extend has been removed here

Anonymous Referee #2

30 **General**

To understand partitioning of (organic) substances in the atmosphere is a key issue. Recently FIGAERO CIMS was developed as a promising method. However to avoid misinterpretations of field and chamber measurements carefully characterization is needed. This manuscript clearly contributes to such a characterization. It addresses the derivation of VP from the conc. maximum of desorption curve in FIGAERO thermograms, utilizing a well characterized reference set of PEGs. The paper is interesting and compact and well written. I suggest publication in AMT after the authors addressed some minor points below.

35

Minor points

p2l7: I am wondering about the Ovadnevaite et al. 2017 reference in the context of gas-phase - particle phase partitioning.

Response: this has been removed from the text

- 5 p2l30: What is the reason / are the conditions for observation of T_{max} ? And related: what is the physics behind the expected (?, Gaussian, p4l47-50) shape of the thermogram? Schobesberger thinks of evaporating particles, but you seem to assume liquid states. Wouldn't the liquids spread and wet the filter fibers? I understand that those details are not really important for the results, but it may help to give an idea/introduction about your imagination of states and processes.

- 10 Response: the state of the material is discussed in reference to the comments of reviewer 1.

p3l37: Something is wrong with this sentence. Please, check and reformulate.

Response: this has been completed

"The evolution of the MS signals from different compounds the filter is exposed to during the Temperature Ramp phase change independently as a function of temperature creating thermograms that are m/z specific."

- 15 p4l13f: "200/300" I don't understand what is meant. 45 min x 6.1° will get you 275° on top of the RT of 25° ,i.e. to 300°C. You may split and separate the info you intended to give into two sentences.

Response: this has now been clarified, as per the request of reviewer 1. Reference to the 300°C measurements have now been removed as no data from these measurements from these experiments have been used in the study.

- 20 p4l29: I don't understand what you want to say here. How can subtraction of a background fit improve instrumental noise. I guess you have to extend here a little bit more.

Response: correct. In response to this and the comments of reviewer 1 a significant improvement in the details of this method has now been included in the supplementary information.

- 25 p4l47: T_{max} for a fragment only reflects T_{max} of the parent compound, if the fragmentation happened after evaporation, i.e. in the gas-phase. However, as far as I understood, there could be also fragmentation - at weak bonds - in the particulate phase, isn't it? Then T_{max} of appearance of the fragment does not represent the thermal properties of the parent anymore. If so, you have to modify this statement in the manuscript accordingly.

Response: this is correct and should also be included. The following has been added to account for this;

- 30 *"There also may be fragmentation of weak bonds in the particulate phase, also giving an unrepresentative T_{max} and desorption profile."*

p5l26: I suggest to include/show this fit in Figure 4.

Response: this has now been added.

- 35 Figure 3: Sample 1-3 where measured during the ramp. Sample 4,5 after the ramp stopped and the system stabilized (at a lower rate of t increase). Does the ramp rate has any effect on the T_{max} ? I guess so. But then sample 4,5, where not measured at same condition as sample 1-3. Please comment.

This variability is now noted in the text and is noted as a limitation in the study

5 *“The same cycle was used for the single component measurements for both the GU and UMan instruments. It is however noted that the analysis provided here does not take into account the possibility of a change in ramp rate affecting the T_{max} . It is therefore recommended that the calibration cycles match that of the measurements.”*

Figure 6, p4l62: I don't understand what is shown here. In the chamber measurement you don't know if the detected formulas are the dicarboxylic acids as tagged? Or did you add the dicarboxylic acids as such. Please, clarify.

10 Response: measurements reported here are the dicarboxylic acids measured during the chamber experiments; this has been made clearer in the text now. These acids were identified through very low errors in the peak peaking and very high repeatability and gaussian shape of the thermograms.

“In addition to the PEG VP calibrations, we also performed FIGAERO measurements of secondary organic aerosols generated in the Manchester Photochemical Aerosol Chamber and vapor pressures of several organic acids (mass accuracy all <2 ppm) from measurements made in these experiments are reported here.”

15 Check co-author name "Krieger" vs "Kreiger"

Response: the manuscript has been thoroughly checked for this mistake and corrected

Check the use of capitals in figure, it should Figure

Response: this has been corrected throughout

Check the use of capitals in peg / PEG

20 Response: this has been corrected throughout

p2l10: 'Such measurements "of are" ongoing. . .'

Response: this has been changes as per the comment of reviewer 1.

p3l9: maybe: "(> 6 month)"

Response: agreed

25 p4l26: too many "averages" here

Response: agreed, the sentence has been rewritten as - *“The average (mean) of the maximum 3 values in the thermogram is used to extract the T_{max} values reported here.”*

p4l49: "mass spectrometry and CIMS" is somehow double, you may want to modify this phrase

Response: correct. Mass spectrometry is deleted from the sentence to only leave reference to CIMS

30 p5l18: "Tmaxes"

Response: this is the correct use here.

p7l12: the "Foley" reference is incomplete

Response: this reference has now subsequently been removed from the main text

Anonymous Referee #3

The manuscript, 'A method for extracting calibrated ...' describes a method of using a series of PEG compounds to calibrate the FIGAERO for determining vapor pressures of detected compounds. The work presents a useful concept that can be used by a growing number of research groups that use the FIGAERO and similar techniques to normalize (or standardize) measurements of the volatility of OA components. The manuscript is succinct, which is nice, but some potentially major details are missing. Please address/clarify the below issues that may affect the applicability of the presented concept, after which the manuscript can be considered for publication.

Specific Comments

A series of PEG compounds was used as calibrants to connect literature VP values of the PEG compounds to FIGAERO T_{max} values. The calibration curve as defined by equation 1 is not shown on figure 4. It would appear to me that a simple exponential curve does not fit the observed values well. Please include the calibration curve on figure 4, and discuss potential reasons for the deviation from the calibration curve.

Response: this was also raised by reviewer one, please see the detailed response there.

The PEG compounds on figure 3 exhibit different desorption profiles, that is, some are much broader than others. Why?

Response: It is not clear why there are different desorption profiles seen in our data. As already noted in past responses whilst significant concentration variability and perturbed ramp rates might lead to such behaviour, our experiments were well constrained and with proper due diligence as highlighted by referee #1.

How were the PEG compounds introduced? Injected? Individually or together? Same heating ramp rate for each PEG? Are the four thermograms of each PEG of the same amount introduced? Have the authors tried injecting widely ranging amounts of a PEG compound?

Response: The PEG samples were manually syringed on to the filter. These were mostly completed individually but one repeat of 4 and 6 and 5 and 8 were conducted together. This is now clarified in the text.

The concentrations used are now discussed in detail as per the request of reviewer 1. The same heating ramp rate is used, the limitation of this is discussed but as a suggestion to other users it is made clear that the same ramp rate for both the calibrations and measurements should be used in order to reduce the effect of this uncertainty.

"The same cycle was used for the single component measurements for both the GU and UMan instruments. It is however noted that the analysis provided here does not take into account the possibility of a change in ramp rate affecting the T_{max} . It is therefore recommended that the calibration cycles match that of the measurements."

How much does the amount introduced affect the T_{max} value? The amount of OA present can affect the T_{max} values, as reported by many FIGAERO users. This issue can severely affect the applicability of the presented technique, thus the T_{max} dependence on OA loading needs to be addressed carefully. Also, please consider plotting signal versus temperature, not time on figure 3.

From the concentrations used in this study there was no dependence observed in either the PEG calibrations or the chamber experiments. We do however agree that the amount of OA on the filter has the potential to affect the measured T_{max} . This is now clearly discussed in the paper. As per the request of referee 1 the ranges of concentrations used for the calibrations are now included in the paper

“As with any calibration it is recommended to use a comparable amount of calibrant material as would be expected to accumulate during the measurements, as it is noted that the amount of condensed material on the filter can affect the T_{max} .”

We do however reiterate that this paper is presenting this as a method to use and the applicability of the PEG series appropriate calibration of the FIGAERO. We do not suggest that equation one can be utilized widely within the community, although our data may provide a useful reference against which others with the ARI FIGAERO may compare.

The main point of the paper is to use a set of compounds that have been identified as a recommended standard for vapour pressure measurement techniques and apply them to the FIGAERO to overcome previously reported uncertainties (Bilde et al, 2015). While we agree that there are factors that can lead to the variability of the T_{maxes} reported here, such as the concentrations used, we feel our method is robust.

I am particularly concerned with the concept of Tmax for compounds like PEG 4, 5, and 8, all of which show very broad desorption profiles. For these species in particular, the amount introduced, heating ramp rate, etc. can affect Tmax values greatly. Perhaps consider reporting the temperature at which half the mass comes off the filter, as opposed to Tmax.

Response: As described we have thoroughly checked all known parameters that may affect the thermograms reported here and we recognise some of the thermograms are slightly broader than expected, nonetheless as a calibration method for the FIGAERO community to use the authors feel that this is an important step to take for using the FIGAERO in this way.

As used in the Stark et al (2017) paper reporting the temperature at which half the mass comes off the filter looks to show good linearity with the T_{max} . Due to the much greater proportion of the community using T_{max} as well as the lack of correlation with concentration and T_{max} observed here, we have chosen to follow this method for the paper. The following has however been added to the paper to show this as a possible method for other FIGAERO users to employ.

“In this study the T_{max} is reported, however an alternative method, “ T_{50} ”, as described in Stark et al., (2017) uses the temperature at which 50% of the signal is desorbed.”

There is brief mention of alpha-pinene oxidation, but no figures are shown and no results discussed. Please elaborate.

Response: We feel that additional information regarding these experiments is not pertinent to the paper we present here, therefore other than including the total mass measured in this study; additional information is not required in this instance.

line 26 page 4 minor manually extracted?

Response: No change has been made to this;

“Due to the relativity small numbers of thermograms analysed from the UMan FIGAERO-CIMS, the T_{maxes} from the Manchester data were manually extracted.”

line 26 page 2, not Teflon (specific to DuPont product), report specific compound like PFA or PTFE

Response: this has been specified in the text