On-line SPME derivatization for the sensitive determination of multi-oxygenated volatile compounds in air

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COMMENTS REVIEWERS

REVIEWER: 2

General comments:

The authors present a study that investigates the application of online SPME-GC-MS for the atmospheric measurement of OVOCs with various functional groups. Therefore, reagents are adsorbed on a fiber and carbonyl functions are derivatized with PFBHA. In the next step hydroxyl and carboxyl groups are derivatized by MSTFA and TMCs. Subsequently, samples are desorbed and analyzed by GC-MS.
The paper presents tests and validation of the method for 11 different OVOCs (8 with carbonyl function and 3 with hydroxy or carboxyl group). The method was applied in the EUPHORE simulation chamber and results are compared to FTIR and PTR-TOF-MS measurements. For example, a good agreement was shown for methylglyoxal measurements. In addition, degradation products of the isoprene ozonolysis were determined. The authors demonstrate that the SPME technique can be used for atmospheric applications and the paper fits in the general scope of AMT.
Although I recommend that this paper be accepted for publication, I have several comments and suggestions that the authors should consider before finalizing this paper.

RESPONSE: We would like to thank the reviewer for their comments and suggestions,

Specific comments:

What is the temperature of the sampling cell? Is any memory effect visible that depends on the history of experiments?

RESPONSE: As was indicate in line 115, sampling cell was under laboratory conditions that implies 20ºC and ambient pressure. We have added this information in the manuscript.
Regarding to memory effect, it was never occurred since all day we start with a SPME blank, SPME and PFBHA blank and no compound was detected in these chromatograms. Also, during methodology development, a blank was done during experiment sequence and no compound was detected, confirming the absence of memory effect. A new short phrase has been included in the revised manuscript.

Line 201 “Also, memory effect on sampling cell was evaluated, including a blank derivatized sampled included on sampling sequence. No compounds were observed, confirming the absence of memory effect”.

Page 7, line 166 and page 9, line 229: Which range of humidity was tested? How was the humidification done?

RESPONSE: Thanks for your comment. Range of humidity test has been now included (0-50% RH). Moreover, a briefly description of humidity addition has been included in line 155 of the revised manuscript.

“Mili-Q water was added by a spryer system (dried cleaned air at 2 bar) into EUPHORE chamber. Dew point system was used to confirm relative humidity values”.

Page 10, line 249: The determination of the precision is described very briefly. Do I correctly understand that for every compound 5 measurements each were performed at reactant concentrations of 25, 50, and 100 ppbv? For some species that is outside of the linear range. Is the precision valid over the whole concentration range used in measurements?

REPONSE: Sorry for the inconvenience. It was a mistake. Precision was estimated from replicate experiments of 1, 10, 25, 50 and 100 ppbV. It was emended in the revised text.

Page 11, line 276: Are there any other methods/instruments (references?) to compare the given SPME performance?

RESPONSE: As has been commented in the abstract and throughout the document, the reference technique for comparing the performance of the SPME methodology has always been FTIR. However, certain limits of detection and quantification, as well as precision and linear range are far from its performance.

Page 12: How did you calculate the dilution in the EUPHORE chamber? Was a tracer used?

RESPONSE: A new paragraph has been included in the revised version (line 155) for clarifying. “The dilution rate in the chamber is calculated from the decay of SF_6 by FTIR areas in the IR range of 762-956 cm^{-1}. The specific dilution process was determined by FTIR adding 120 $\mu g\ m^{-3}$ of SF_6 as a non-reactive tracer (value of $1.1\times10^{-5}\ s^{-1}$) to the reaction mixtures at the start of the experiments”.

Page 12, line 287: From the different OVOCs, we selected methylglyoxal since was previously selected such as OVOC model. This sentence sounds very odd and the meaning is not clear to me. Please rephrase.

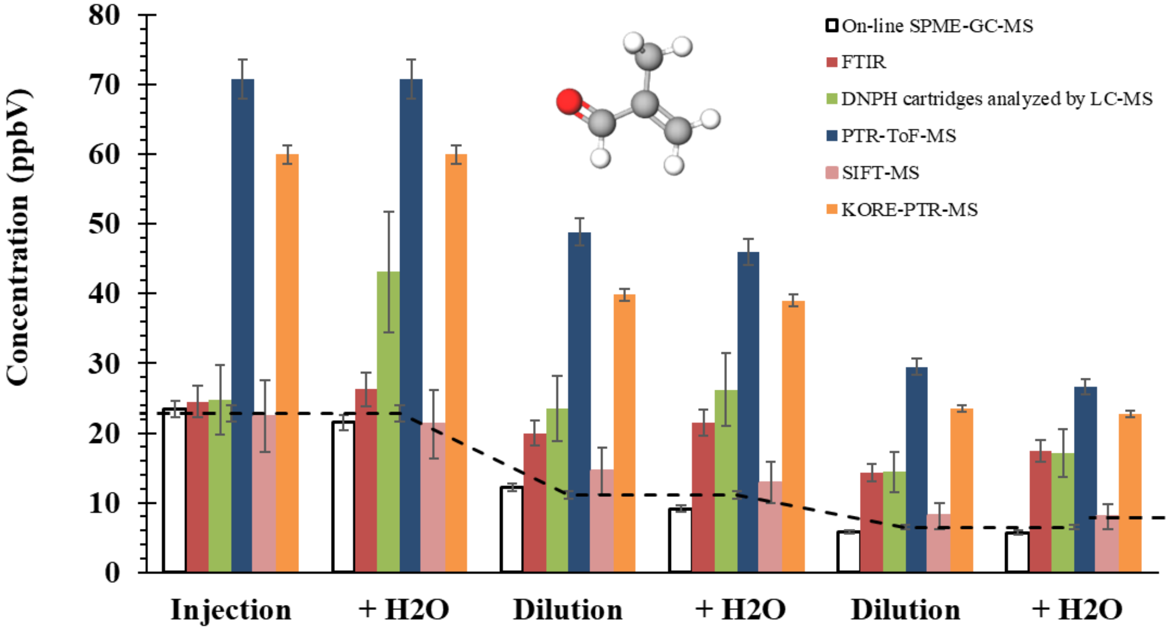
RESPONSE: We have rephrased it. “From the different OVOCs, we selected methylglyoxal since was previously used as OVOC model (see section 3.1)”.

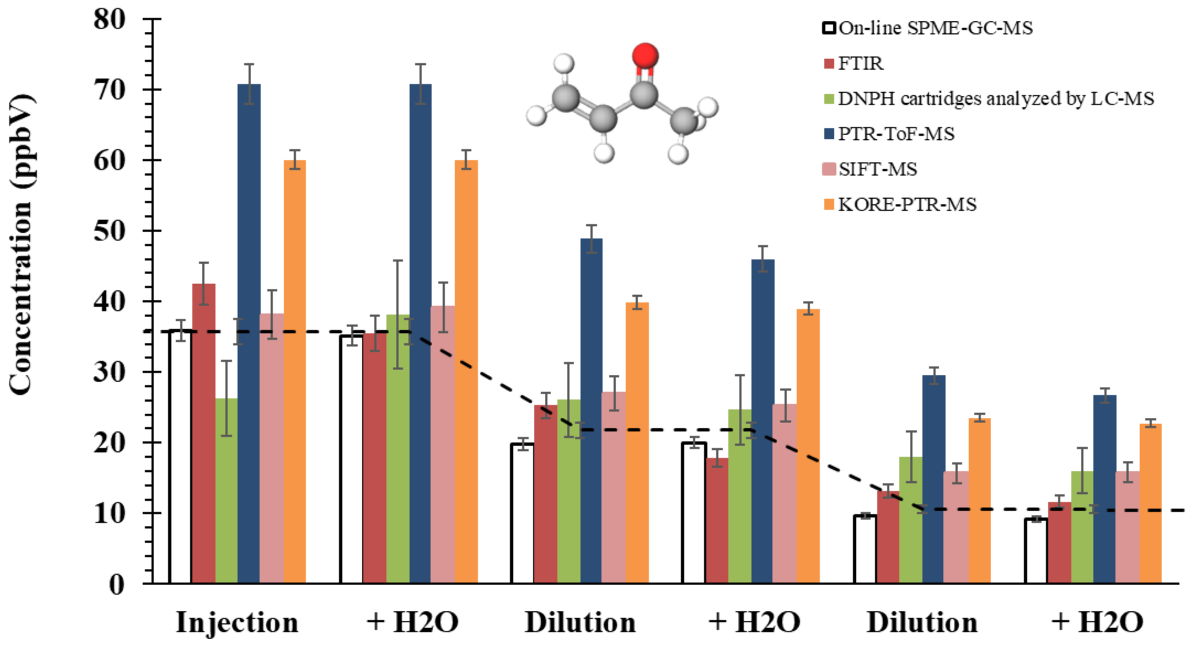
Page 12, line 288: Here the authors state that other techniques suffer large interferences. Two sentences later, it is written: “As can be observed, the results from SPME-GC-MS plus derivatization technique were in great agreement with the theoretical values […] and with the results obtained by other techniques […].” Please specify which interferences and other techniques you are talking about.

RESPONSE: Ok thanks. As discussed at the beginning of the section, the interferences are “high humidity, and dilution steps can induce in the methodologies evaluated in this work (see Table SI.1)”. The interferences are described: relative humidity and dilution process. The techniques are those that appear in table SI1 that are PTR-ToF-MS and SIFT-MS -spectroscopic techniques – and DNPH cartridges analyzed by LC-MS – off-line technique-.

Page 12, line 303: In Fig. 3 a) and b), SPME-GC-MS measurements do not agree with theoretical calculations within the stated uncertainty. It looks like measurements underestimate theoretical calculations up to 30%. That should be addressed in the manuscript.

Sorry it was a mistake when theoretical concentration was plotted. The correct figure 3 are:





Page 12, Fig. 2: The reader would benefit from simplified labels instead of looking them up in the caption. Exchange labels "tech.2" and "tech.4" by FTIR and PTR-ToF-MS, respectively.
Page 13, Fig. 3: See comment to Figure 2 for labels tech.2, tech.4, and so on. How do KORE- and Ionicon-PTR-ToF-MS correspond to FZJ and Leeds instruments listed in Table SI.1? Please use a uniform nomenclature.

RESPONSE: Thanks for your comments. It was emended in the revised manuscript and new figures were done.

Section 3.6 needs some attention. The content is not very clear and it needs a carful language check. See the following comments.
Page 13, line 324: The results fitted to a standard growing for degradation products. The meaning of this sentence is not clear. Please rephrase.

RESPONSE: Thanks. It was rewritten. "The degradation rate of isoprene and ozone was fitted to first order decay as previously described in Karl et al., 2004".

Page 13, line 325: In case of 2-butanone, the formation was fast and, after 1 h, a further transformation was registered. I don't think that transformation is the right word here. What you want to say is that 1) 2- butanone is formed and 2) after 1 h, the 2-butanone is consumed. Do you have an idea what causes the strong loss compared to the other measured VOCs?

It is true, we have changed this sentence. “In case of 2-butanone, the formation was fast and, after 1 h, a decay by chemical degradation was registered”. However, we have not made a study atmospheric degradation mechanism because it is beyond the objective of this work

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Page 13, line 328: Which OVOCs were identified? Can you give some examples of how good the agreement is? Did you compare measured time series to a chemical model (which one?)?

RESPONSE: OVOC identified is included: methyl vinyl ketone. We compare our data with provided by Karl et al., 2004; Wennberg et al., 2018 in the literature.

Page 14, Fig. 4: What is the meaning of the solid lines in b)? Is a fitted function? Which type of?

RESPONSE: It was only to clarify the growth of methacrolein, glyoxal and methylglyoxal and the different behaviour of 2-butanone.

Technical comments:

REPSONSE: All technical comments list below have been accepted

Page 3, line 43: Their tropospheric range levels are highly variable… better use: Their tropospheric concentrations…
Page 5, line 111: …losses of steady OVOCs.I think you mean “sticky”
Page 7, line 162: … proton transfer time of flight mass spectrometer (PTR-ToF-MS), …
According to Table SI.1, two PTR-ToF-MS instruments were used.
Page 10, line 243: PTR-ToF-MS
Page 10, line 243: Michoud et al., 2018 is not listed in the references. Please check references.
Page 10, Table 3: Please use uniform names in text and tables. In table the authors use L.D., L.Q., and RSD. In the text, LOD is used for limit of detection. Abbreviations for L.Q. (quantification limit) and RSD (relative standard deviation) are not introduced. Same applies to Table 4.
Page 12, line 288: … presented great interferences. Replace by “large”.
Page 12, line 293: … a test t…Remove “t”.
Page 13, line 323: Regarding to minority products, the OVOCs determined were 2-butanone,methacrolein, methyl vinylketone glycoladehyde, hydroxyacetone glyoxal and methylglyoxal. I suggest replacing minority by minor. Please check for missing commas.
Page 13, line 326: The maximum concentrations were… I would suggest rephrasing “Measured 2-butanone concentrations were…
Page 14, Fig. 4: In the caption, do you mean “top” = a) and “bottom”= b) ?

Sorry for these mistakes. All of them has been solved in the revised manuscript.