

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

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RESPONSE TO THE REVIEWS

REVIEWER: 1

15

General comments:

The paper addresses innovative methodology related to measurement of relevant gaseous compounds in a simulated atmosphere. This is compliant with the very scope of AMT.

20 *The paper is the sum of excellent quality work and I would recommend it as a valuable asset for researcher performing simulation chambers experiments.*

The experimental work and the own contribution are well embedded in the frame of theoretical description of the analytical techniques used and suits fully the scope of the research. More, the description of the experiments is detailed sufficiently to allow duplication of the results. A clear structure makes the content readable and understandable.

25 *The literature references are extensive but not in excess.*

However, a few paragraphs need more attention due to overseen minor language errors. This is valid for figure captions as well. These are listed below in the section “technical corrections”.

30 *The supplementary material is supportive and complete the main body of the paper with concrete experimental data. However, at this stage the supplementary part needs corrections. They are listed below, in the “Technical corrections” section.*

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

Specific comments:

40 Lines 149 – 151: *There is no indication for the reference values for FTIR absorption cross-sections used here. Could be possible to indicate the source of these values? Or, if the quantification was based on the amount of compound introduced in the chamber?*

45 RESPONSE: Thanks for your comment. The new paragraph is: “Second, a White-type mirror system (path length of 553.5 m) coupled to a FTIR with MCT detector (NICOLET 670, Thermo Scientific, USA) was used. Spectra were collected at 1 cm⁻¹ resolution by averaging 300 scans (sampling time: 5 min). The quantification was based on aldehydic C-H stretching for methylglyoxal, within the spectral region of 2750–3000 cm⁻¹ and C-C and CH₂ bands for isoprene, methyl vinyl ketone and methacrolein in 900 – 1047 cm⁻¹ by using ANIR software (Ródenas, 2008). Calibrated references used in the analysis are found at the LAR database.”

50 New reference has been included. Ref: LAR - Library of Analytical Resources: IR Spectra. Database of Atmospheric Simulation Chamber Studies of the EUROCHAMP-2020 Project. <https://data.eurochamp.org/data-access/spectra>.

55 *Was the gas-phase composition for all analysed compounds constant over 6 hours?*

60 RESPONSE: No. Concentrations of OVOCs compounds were corrected by dilution, an intrinsic process on simulation chambers. Reactants and products are diluted during experiments and to determine the correct concentration values, they must be corrected. The dilution rate in the chamber is calculated from the decay of SF₆ by FTIR areas in the IR range of 762-956 cm⁻¹. The specific dilution process was determined by FTIR adding 120 µg m⁻³ of SF₆ as a non-reactive tracer (value of 1.1×10⁻⁵ s⁻¹) to the reaction mixtures at the start of the experiments.

This information will be added to the manuscript

65 Line 195: *To what refers “no-incubation time”? According to figure 1, in an incubation cell occurs the doping of fibers with PFBHA. Please clarify.*

70 RESPONSE: Thank you for your comment. What we want to explain, and which is thus shown in Figure 1 is that the derivatizing reagent PFBHA does go through an incubation process in a cell at 50°C but the sampling occurs in the sampling cell where the temperature is the same that the temperature of the simulation chamber.

Line 210: *How good is the separation/determination of methacrolein and MVK in a mixture since they seem so alike? (m/z, retention times).*

75 RESPONSE: The separation is very suitable because the oximes product of derivatization with PFBHA have quite different retention times. Individual standards were prepared to identify the oximes of each compound (as shown in Table 2). Methacrolein has 2 oximes with rt 7.2 and 7.3 while MVK has 2 oximes at 7.5 and 7.6. The chromatographic peaks with the largest area and the most reproducible are selected, which are the peak of rt 7.2 for methacrolein and rt 7.5 for MVK, with which the differentiation
80 is adequate and allows a correct quantification.

Line 325: ...In case of 2-butanone, the formation was fast and, after 1 h, *a further transformation* was registered. This suggest that previously another transformation took place?

85 **RESPONSE:** Sorry for the inconvenience. It was a mistake. Sentence has been modified: In case of 2-butanone, the formation was fast and, after 1 h, a decay by chemical degradation was registered.

Lines 291-292: *compound was introduced into EUPHORE chamber - and with the results obtained by other techniques, both *optical* and *spectroscopic* methodologies. I would suggest “both optical and mass spectroscopic methodologies”.* FTIR is a kind of spectroscopy, though.
90

RESPONSE: Thanks. The sentence has been included in the revised version.

Please verify the names of the compounds in the main body and supplementary material. There are some inconsistencies as the compounds are not named in the same way overall in the paper. More, in the Supplementary material the names, structures and mol masses are not always correct indicated (s. list in the Technical corrections section).
95

RESPONSE: Thanks for the comment. We have checked names and nomenclature along the revised draft.
100

Technical corrections:

RESPONSE: We accept technical corrections listed below. They will be included in the revised version.
105

In addition specific responses to comment on line 133: 100 °C min⁻¹ is correct. We have a fast GC-MS The sentence in line 233 should be replaced by : It has been changed to OVOCs air mixtures at different concentrations were analyzed - ranged from 5 pptV to 100 ppbV
110

The sentence in line 277-279 should be: In conclusion, double derivatization treatment allowed the proper determination of OVOCs, independently of the functionalized group (-C=O, -OH and/or -COOH), even carbonyl compounds with α -hydrogen
115

Line 345. No we want to mean multifunctional compounds

Main paper body:

Line: 55 “lab-on-chip” should be replaced by “lab-on-a chip”, for consistency.

Line 95: ...*E-butenedial*...

Line 111: “Sampling line was of sulfinerTR material and it was heated at 80°C to avoid losses of *steaky* OVOCs compounds.”
120

I am sure the intended word was “sticky”. Please replace.

- Line 133: for 2 min, then ramped at a rate of 12 °C min⁻¹ to 240 °C, 100 °C min⁻¹ to 280 °C.
I wonder if here is really a rate of 100 °C min⁻¹ and not 10 °C min⁻¹ ?
- 125 Line 196-197: ...Selected conditions (10 min at 250 °C) assured high efficiency, calculated from peak areas of methylglyoxal derivatives (13.9 min, 14.2 min, 14.4 min, 14.5 min) being negligible the underivatized peak (retention time 7.65 min).
This sentence needs attention as it is unreadable.
Line 206: *the* selected compounds
- 130 Please add the article before “selected”.
Line 220-221: reduced and perfectly resolved (resolution > 1.5). The calculated recoveries ranged from 91% (glutaraldehyde) *and* 99.7% (methylglyoxal) as shown in Table SI. 2.
Please replace “and” by “to”.
- 135 Line 227-228: The effect of humidity was examined because several techniques such as PTRMS-TOF or CEAS showed an erroneous determination for air samples with high water content, *depends* on the applied data evaluation routine (Talman et al., 2015).
Please change into “that depends” or depending”.
- Line 233: Air mixtures at different concentrations were analyzed concentration range from 5 pptV to 100 ppbV.
- 140 This sentence needs attention as it is unreadable.
Line 277-279: In conclusion, double derivatization treatment allowed the proper determination of OVOCs, independently of the functionalized group (-C=O, -OH and/or -COOH), even with α -hydrogen.
This sentence needs attention as it seems incomplete.
- 145 Line 286: potential interferants, such as high humidity, and dilution steps can induce in the methodologies *evaluated* (see Table SI.1).
Please decide if after “evaluated” should come an “here” or “in this work”. Otherwise “evaluated” should precede “methodologies”.
- Line 288: From the different OVOCs, we *selected* methylglyoxal since was previously *selected such as* OVOC model (see section 3.1).
- 150 I would suggest: From the different OVOCs, we selected methylglyoxal since was previously used as OVOC model (see section 3.1).
Lines 306-309: ... In this the sum of MVK and MACR are measured *due to* PTR- MS methods are not selective. Both compounds have different sensitivity factor imposing an additional inaccuracy on the data, for more details see Rodenas et al., in preparation, 2021. On the contrary, *the* on-line SPME-GC-MS
- 155 approach can be used for a reliable monitoring of atmospheric reactions.
I would kindly suggest the revision of this fragment as it is not easily readable.
Figure 3: Please replace “*top*” and “*bottom*” by “*panel a*” and “*panel b*”, respectively.
Figure 4: Please replace “*top*” and “*bottom*” by “*panel a*” and “*panel b*”, respectively. As only HCHO is produced, the second sentence should read “Reagents and main *product* determined by FTIR (panel
- 160 a).”
- Line 342: Please replace with “*Conclusions*”
- Line 345: ... for alcohols, aldehydes, ketones, carboxylic acids and their *combinations*, ...
Do you think that here “mixtures” could be more appropriate? If not, please ignore this comment.
- Line 360: ...This article is part of the special *is-sue* ...

165 *Please delete the hyphen.*

SUPPLEMENTARY INFORMATION

170

RESPONSE: We accept all the changes suggested below. They will be changed in the revised manuscript.

*Please correct the title of the: **SUPPLEMENTARY** INFORMATION part.*

175 Table SI.1: *Do you think that merging the cells in the column corresponding to CEAM foundation and CEAM, respectively, would make it easier to read?*

Figure SI.2. *Please correct the mol mass of methylglyoxal (72 instead of 74) and E-butenedial (84 instead of 86). Please draw the correct structures for glutaraldehyde and 4-oxo-2-pentenal.*

Figure SI.3.:

180 d) *The mass 54.1 is present in the MS spectra although is missing in the frame.*

i), j) *Please correct the mol mass of methyl glyoxal as 72.*

k), l) *The presented structure corresponds to succinaldehyde. To be glutaraldehyde needs one more C. Please correct it accordingly.*

m), n) *The presented structures correspond to 2-buten-2-methyldial, not 4-oxo-2 pentenal.*

185 *More, the peaks in the chromatogram in panel m) are labelled overall as 4-oxo-2 pentanal. Please make the corrections according to the right compound.*

o), p) *Please correct the name as E-butenedial. Please correct the mol mass of E butenedial as 84.*

190

REVIEWER: 2

General comments:

195 *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.*

200 *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.*

205 *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,

210 **Specific comments:**

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

215 RESPONSE: As was indicate in line 115, sampling cell was under laboratory conditions that implies 20°C 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.

220

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”.

225

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

230 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”.

235 *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?*

240 REPOSE: 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?

245 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.

250 *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 SF₆ by FTIR areas in the IR range of 762-956 cm⁻¹. The specific dilution process was determined by FTIR adding 120 μg m⁻³ of SF₆ as a non-reactive tracer (value of 1.1×10⁻⁵ s⁻¹) to the reaction mixtures at the start of the experiments”.

255

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)”.

260

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.

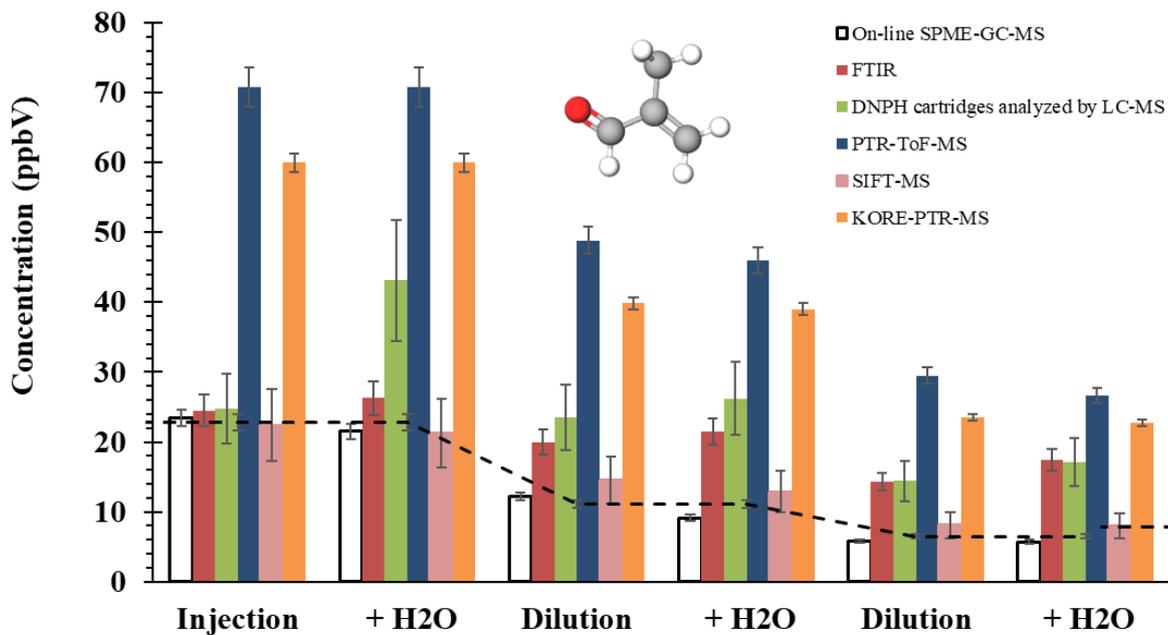
265

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-.

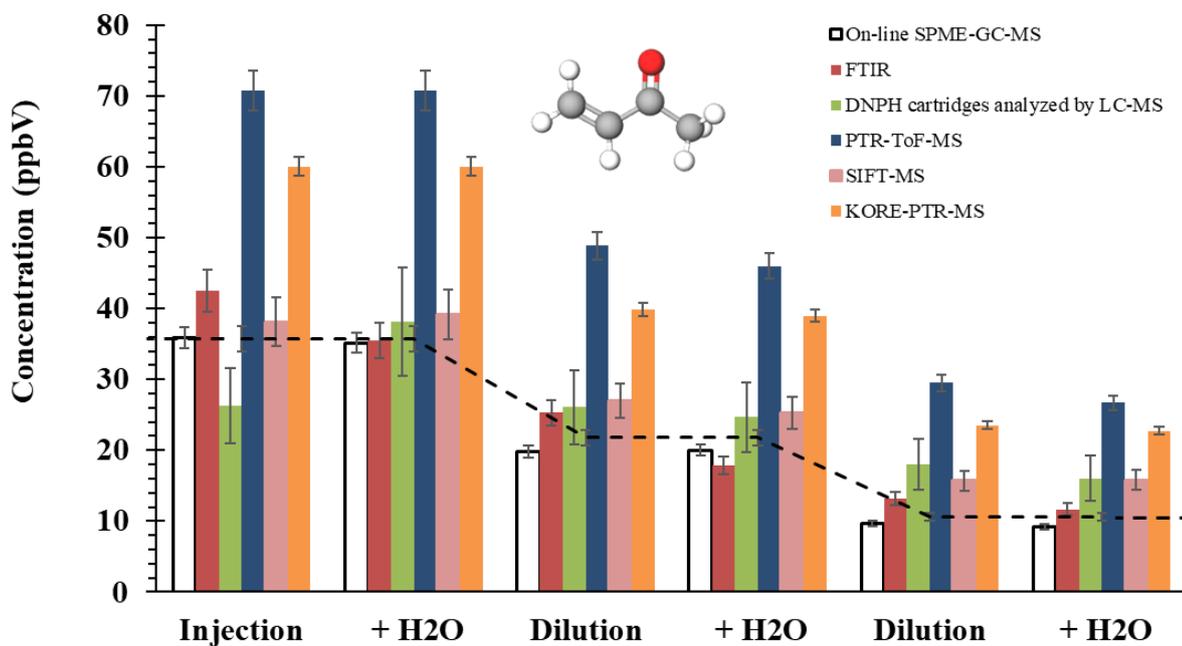
270

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:



275



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.

280

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.

285 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 careful language check. See the following comments.

290 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”.

295 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?

300 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

305 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.

310 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:

315 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...

320 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.

325 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".

330 Page 13, line 323: Regarding to minority products, the OVOCs determined were 2-butanone, methacrolein, methyl vinylketone glycolaldehyde, 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..."

335 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.