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

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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.

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.

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”.

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.

Specific comments:

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, how was ensured that this occurred without loses?

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

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.

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

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?

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.

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).

**Technical corrections:**

**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 sulfinert® material and it was heated at 80°C to avoid losses of steaky OVOCs compounds.”
*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\(^{-1}\) ?*

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
*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”.

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.
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.

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).

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 Ródenas et al., in preparation, 2021. On the contrary, the on-line SPME-GC-MS 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 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…

Please delete the hyphen.
SUPPLEMENTARY INFORMATION

Please correct the title of the: SUPPLEMENTARY INFORMATION part.

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.: 

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. 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.