

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

5 Esther Borrás¹, Luis Antonio Tortajada-Genaro², Milagro Ródenas¹, Teresa Vera¹, Thomas Speak³, Paul Seakins³, Marvin D. Shaw⁴, Alastair C. Lewis⁴, Amalia Muñoz¹

¹ Fundación Centro de Estudios Ambientales del Mediterráneo (CEAM), 46980 Paterna, Valencia, Spain

² Departamento de Química-Instituto IDM. Universitat Politècnica de València, 46022, Valencia, Spain.

10 ³ University of Leeds, LS2 9JT, Leeds, UK.

⁴ National Centre for Atmospheric Science, University of York, York YO10 5DD, UK.

Correspondence to: Amalia Muñoz (amalia@ceam.es)

COMMENTS REVIEWERS

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REVIEWER: 1

General comments:

20 *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.

25 *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.

30 *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.

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?*

RESPONSE: Thanks for your comment. The new paragraph is: “Second, a White-type mirror
45 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
50 in the analysis are found at the LAR database.”

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?*

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
60 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.*

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
70 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

80 selected, which are the peak of rt 7.2 for methacrolein and rt 7.5 for MVK, with which the differentiation 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.

90 *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.*

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

95 *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).*

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

Technical corrections:

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

In addition specific responses to comment on line 133: 100 °C min⁻¹ is correct. We have a fast GC-MS
110 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

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.

120 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."
- 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.
- 125 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.
- 130 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".
- 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
- 140 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.
- 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*
- 150 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,
- 155 for more details see Rodenas 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
- 160 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.

165 Line 360: ...This article is part of the special *is-sue*...

Please delete the hyphen.

170 SUPPLEMENTARY INFORMATION

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

175 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.

180 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.

185 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.