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Atmospheric Measurement Techniques Discussions

Interactive comment on "An *in situ* gas chromatograph with automatic detector switching between Vocus PTR-TOF-MS and EI-TOF-MS: Isomer resolved measurements of indoor air" *by* Megan S. Claflin et al.

Anonymous Referee #2

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Claflin et al. demonstrate a novel dual-channel TDPC-GC-EI/Vocus(H_3O^+)TOFMS instrument. The combination of chromatography with preconcentration, soft and hard ionization methods, highly time and mass resolved time-of-flight detector makes it probably the most universal and comprehensive state-of-the-art instrument currently available for time-resolved isomer-speciated VOC measurements. These measurements are particularly needed in the field of air quality and indoor and outdoor atmospheric chemistry. This manuscript shows a significant improvement in quantified chemical completeness, time resolution, and molecular speciation thanks to enormous

synergy from coupling complementary state-of-the-art analytical methods. While I can see some potential for further improvement, overall, the manuscript is well written and, in my opinion, will be a valuable contribution to the fields of gas chromatography and mass spectrometry for indoor and other atmospheric applications. I would have relatively minor comments and suggestions which hopefully can be easily addressed in the revision.

Specific Comments and Suggestions

1) The title reads nicely exhaustively informative but the presence of "indoor air" in the title might be misleading. I interpret the novel instrument/method as more generally applicable than just for the indoor air but perhaps the title might mislead the AMT audience that the method/instrument is dedicated only to indoor air measurements rather than that the indoor air was just the indoor gym field example. The extremely impressive detection limit thanks to the Vocus sensitivity and preconcentration makes this method particularly powerful for discoveries also in the outdoor atmosphere and many other contexts.

2) I think the novel instrumentation presented in this paper is absolutely outstanding, but I do have a feeling that the capabilities are *much* greater than described in the manuscript. The table 2 nicely shows different classes but with the sub-ppt detection limit indoors one would expect thousands of ions. Are the compounds in Table 2 just select, example compounds from the weight room or was it meant to represent the complete chemical composition?

3) The paper focuses predominantly on monoterpenes, select aromatics and silicon-containing VOCs (cVMS, DMSD). This is great but I would recommend expanding beyond the weight room, on the detectable compounds, ideally across a range of c*, and chemical classes. It would also be nice to add to the discussion which compounds are not detectable or are particularly challenging.

4) I really appreciate the switching capability between the RT-Vocus, GC-Vocus and

GC-EITOF. The “automatic detector switching” is emphasized already in the title. However, I could not find information how fast the switching is and how the data between switching is treated/trimmed. It would be great to include this information.

5) One big issue, not specific to this paper, but applicable to analytical chemistry methods in general are potential chemical conversions in the instruments or sampling system due to contact with materials (e.g. metal surface) or thermal (e.g. high temperature ramp or desorption). The authors are in an excellent position to shed some light on this question because RT-Vocus and GC-Vocus data can be directly compared for compounds which would be expected thermally unstable. I think expanding on this general issue could be interesting for the AMT community.

6) 100 ppq LOD for mp-xylenes is certainly extremely impressive! While 1 ppt for o-xylene is still impressive, I wonder what exactly is causing a large difference in LOD between those isomers.

7) Two units are used for the normalized signals (ncps, and ncts). The text cautions the reader about the differences which helps. The normalization process is well described in Sect. 2.9. It seems that the ncps normalization was done by the second water cluster which makes me wonder if the signal was relatively constant in the Vocus at the given E/N ratio and unaffected by sample humidity. Is it assumed that this ion would reflect changes in H3O+ more than the changes in ambient H2O? Because changes in the E/N ratio would largely affect ncps values normalized to humidity-independent water cluster I would suggest adding a subscript with E/N ratio used (e.g. Sn_{150Td}). This should allow for comparisons in future campaigns and prevent confusion of normalized sensitivities derived at different E/N ratios. I would also suggest showing in addition (maybe in parenthesis) the absolute sensitivity (cps/ppb).

8) Further to the comment above, I have been missing some details on the Vocus operation and data processing. The reader is referred to the paper by Finewax et al. (2020) but this paper does not seem to be published yet so I could not refer to it. It

is great to see the parameters for the IMR, but it is unclear if the TPS voltages have been optimized with the Thuner or manually. I am also specifically wondering why 1.5 mbar of IMR pressure was used? It is not an issue but usually >=2 mbar is used. The E/N ratio of 150 Td is already somewhat high so the higher pressure could lower it and further boost the sensitivity but if there was a specific reason perhaps it could be interesting to include.

9) It is nice to see the good performance of the GC-(PTR)Vocus channel. For instance, the speciating power of monoterpenes looks simply excellent. In terms of the other isomeric mixtures, would there be any benefit from using GC-(NH4+)Vocus ionization or has it not been tried yet in this configuration? Perhaps it could be inspiring to add some prognosis on this to the future work.

10) By looking at the detected compounds in the indoor campaign (Table 2) I am missing more highly oxygenated compounds such as acids, hydroxy acids. Would it be useful to try the instrument with an in-situ derivatization (e.g. Isaacman et al., 2014)? Other compound families I am wondering about detection/speciation by this GC are sulfur-containing, amides, amines, heterocycles, metalorganics. By comparing the data from the GC-Vocus and RT-Vocus, it should be possible to delineate the groups of compounds which may not have made it through the column.

11) It is great to see GC and Vocus synergistically complementary. I understand that Finewax et al. (2020) is going to report expanded Vocus dataset from the gym, but I wonder why D5 is shown as detected by GC-EITOF but not GC-Vocus (Table 2). It is surprising because Vocus is definitely very sensitive to D5. Could it be that the sample did not reach Vocus for some reason? What was the detectability of D6 and D7?

12) L365 The use of “artifacts” term in this context reads extremely misleading here. The fragments or clusters are typically not artifacts in PTRMS. In many cases they can be used to quantify compounds (e.g. the cyclohexadiene fragment of monoterpenes m/z 81.0699 or methanol cluster m/z 51.0446). I suggest replacing with “interferences”

or “complications” to avoid confusion with artifacts from sampling tube materials, etc.

13) The DMSD story is very well done. Clearly this discovery would have been much more difficult without the complementary power of this instrument. However, I am completely unconvinced by the indoor OH radical hypothesis. It simply does not make sense to me in terms of Fig 4 showing increase in concentration over night and being correlated with RH. This does seem perfectly aligned with a possibility of microbial biodegradation of siloxanes in PCPs in sweat. It would be consistent with numerous sources reporting it as a biodegradation product (Accettola et al., 2008; Xu, 1999). While this explanation seems most likely to me for this indoor air case, it does not necessarily mean that DMSD is not formed via OH oxidation outdoors which would be another example of an analogy between the atmospheric and microbial oxidation/degradation.

14) The quantified speciation of monoterpenes by GC-Vocus is extraordinarily skillful. These instruments are perfectly suited to contribute to a progress in source apportionments between anthropogenic, plant, fruit, and microbial sources of this important group of compounds. I strongly suspect but it would be great to know if the instrument is also capable of speciating sesquiterpenes.

Technical

15) In several places a number and a unit are not separated by a space.

References:

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