

Interactive comment on “Low-pressure gas chromatography with chemical ionization mass spectrometry for quantification of multifunctional organic compounds in the atmosphere” by Krystal T. Vasquez et al.

Anonymous Referee #1

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Reviewer comments on Vasquez et al., "Low-pressure gas chromatography with chemical ionization mass spectrometry for quantification of multifunctional organic compounds in the atmosphere"

The authors present here a new instrument for the chromatographic separation and analysis of labile compounds of interest to the atmospheric chemistry community, in particular many known oxidation products of isoprene. The instrument is technically sound, relatively thoroughly described, and has the potential to significantly advance our understanding of the atmospherically-important isoprene oxidation system. I have

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only minor concerns regarding the scientific or technical aspects of this work, but find there are a few larger issues regarding the overall presentation, leading me to recommend publication following major revisions addressing the comments below.

General comments:

1) Sections of the instrument description are not clear. For example, from the diagram in Figure 1 it is not clear to me what the sample flow path is or where the sample is actually collected. Is it pulled straight through the entire column, or is it trapped on the 4-port valve? What is the purpose of pump M? What is the purpose of flow tube F? A few more of these sorts of questions come up throughout the comments below.

2) Sections of the instrument calibration are not clear. For example, it is mentioned that some compounds have sampling losses, but then there is no further mention or discussion of this. Calibration appears to rely in some way on a different c-ToF, but exactly how that is being used is not clear. It sounds like not all compounds have authentic/synthesized standards, and if not, how are retention times determined? Estimating collection and transfer efficiency by comparing GC-CIMS signal to CIMS signal likely suffers from an assumption of equal transmission of all isomers, but it is not clear if that is being accounted for because there is little discussion of how it is being applied.

3) Demonstrating the capabilities by field deployment is a valuable addition, but the authors seem to be focusing more on the actual isoprene oxidation chemistry and science than in thinking about this as a proof-of-concept. Several detailed chemical questions regarding unimolecular reactions, etc., are addressed and discussed all within a few short paragraphs, which does relatively little to advance the instrumentation aspect of the paper, but is also too detailed and dense to give a good discussion of the scientific advances. My strong recommendation is focus on this section only as a proof-of-concept. For instance, a major advantage of this technique is the time-resolved data yet the authors show no timeseries of concentrations or isomer ratios, or demonstrations of the continuous operation other than inferring it from the diurnal patterns.

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Overall, all three comments are sort of different sides of the same coin - my impression is that the authors seem to be skipping past or over some key instrument issues (in part by relying heavily on the supplementary information) in order to get to the science, and in doing so are not quite giving either side of the story the attention they deserve. I think the approach is sound, believe it is well tested, and am excited by the scientific prospects, but I think better organization and focus would better serve both the instrument descriptions and the science.

Technical comments:

Page 2 line 3: "can also lead to a scenario" sounds a bit odd to me, maybe just "Chemical oxidation can cause OVOCs to increase....".

Page 2 line 5: Use "In addition" or "also", but probably not both

Page 2 line 27: The GC paragraph sounds like it is about GC in general, in which case it would be a much larger discussion. I think the authors are mostly discussing field-deployable/in-situ GCs here, which should be made clear.

Page 2 line 30-31: Though I realize it is not possible to make this list of GC-based OVOC measurements comprehensive, there are a few absences that stand out. I would include some of Allen Goldstein's measurements in this list, perhaps Millet et al., JGR 2005 which saw MVK and methacrolein as well as other OVOCs, and arguably SV-TAG as I believe it can see many oxygenated gases (Zhao et al., AS&T 2013). I would also include the NOAA GC, such as Goldan et al., JGR 2004, and/or some of Jessica Gilman's work.

Page 3 line 22: I don't understand how the air is subsampled. Is there a sample loop or something? Oh, on the head of the column - so is there a valve in the CIMS interface? There needs to be some more clarity on how sampling happens

Page 3 line 17: What is "Low pressure" about it? It seems like a regular GC approach to me: trapping cold, then heating and pushing through N₂ to a vacuum detector. I

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gather the "LP" aspect is the large bore column, which reduces carrier gas pressures? A short mention or discussion of this would be helpful.

Page 3 line 28: The compounds aren't separated by the temperature controller, they are separated by the GC, using a ramp controlled by the controller.

Page 3 line 29: "each plate" is not that clear. Do the author's mean "on either side of the GC manifold/housing"?

Page 3 line 30: What is the purpose of the flow tube? It makes a big difference later, but it's not clear what the function is. I would think interaction with ions, but seems to happen latter.

Page 6 line 16-21: FT and HS is asymmetric naming, with one after the approach and the other after the result. FT and IS (ion source) would be preferred,

Page 6 line 23: It's not clear why introduction at the source causes longer interaction times. Does fragmentation affect/complicate calibration?

Page 7 line 14: When the authors say "directed" do they mean direct sampling, or analysis by GC? Given the fragmentation in the HS method, it seems to me that the latter is necessary.

Page 7 line 15: Which standards are available/synthesized and which are not? Later, for instance in Figures 7, 10, and 11, the author's seem to know the elution orders of many specific isomers - are these all from authentic or synthesized standards?

Page 7 line 16-20: It is not clear what the purpose of the c-ToF-CIMS is, or where it is discussed or first mentioned. Is it that there are known sensitivities with that instrument, so that is the purpose of the average sensitivity difference? How does it help to compare to the c-ToF? This paragraph needs generally more explanation to be made clearer.

Page 8 line 27: for which species are losses observed?

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Page 9 line 2-3: This is an interesting approach that potentially provides very nice confirmation of compounds for which standards aren't available. However, do the author's know that all isomers are transferred equivalently, and that all isomers can be seen? If total isomer-resolved signal is less than direct CIMS signal, that could be due to incomplete transmission of all isomers as seems to be implied by the author's, but it could also be due to complete transmission of one isomer but not the others, or complete transmission of all observed isomers but the presence of non- or poorly-observed other isomers. It is not clear to me that this approach fully works, and no effort is made to validate it here.

Page 9 Section 3.2: Dilution will solve the humidity problem, but only reduces and does not solve the problem of reactions on the adsorbent from ozone or other oxidants. To collect these compounds, an ozone scrubber is probably out of the question, but have the author's done any tests to evaluate the impact of ozone on these compounds under typical sampling conditions?

Page 10, Section 4: How long were these campaigns and/or measurement periods?

Page 10, line 18: "Isomers" is a more common term than "mass analogous", or the authors could use "isobaric", the mass spectrometric term for having the same mass

Figure 3d-f: Both axes are CIMS signals, but one is labeled normalized IHN signal, and the other as CIMS signal. Why not label the right as m/z 104 signal, or water signal or something comparable?

Figure 8: The period of GC elution (black line) seems to have significantly lower scatter, even during background periods - is that real, and if so why is that?

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