

***Interactive comment on* “Evaluating the performance of five different chemical ionization techniques for detecting gaseous oxygenated organic species” by Matthieu Riva et al.**

Matthieu Riva et al.

matthieu.riva@ircelyon.univ-lyon1.fr

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Anonymous Referee #3

General comments: Many previous works discussed the performance of chemical ionization instruments in detecting oxygenated compounds but few of them systematically compared each other. This manuscript comprehensively evaluates the capability of five widely-deployed chemical ionization techniques in the molecule identification, the range of oxygenated species that can detect and the sensitivity under different conditions. The results can be extremely useful for future studies using these mass spectrometry techniques. I recommend the manuscript to be published in AMT after the

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following comments are considered.

We thank the reviewer for careful consideration of our manuscript.

Individual comments:

Line 50-51 “While specifically shown for the case of α -pinene ozonolysis, we expect our general findings to be valid also for a wide range of other VOC-oxidant systems.” This can be important, but I do not see much discussions on this.

We added a paragraph detailing this argument from the abstract. Lines 629-637: “The results in Figure 6 are based on the α -pinene ozonolysis system. While we will not speculate too much about the extent to which these findings can be extrapolated to other systems, certain features will remain similar also for other atmospherically relevant reactions. For example, the most oxidized gaseous HOM species will likely have been formed through autoxidation processes, which means that they will contain hydroperoxide functionalities, and could thus be detectable by the Nitrate. Likewise, the HOM, and in particular the dimers, will very likely have low volatilities, requiring high sample flows with minimal wall contact, as in the case of the Eisele-type CI inlets used in the Nitrate and Amine. Several other key features are also expected to be valid in different VOC-oxidant systems, and therefore we believe that our findings are relevant also for many other reaction partners.”

Line 230-232: “For the PTR instruments and Iodide, a duty cycle correction was applied ... due to the orthogonal extraction of the mass analyzers.” Why only for PTR and Iodide CIMS? Why not for nitrate and amine CIMS. Please explain.

A duty cycle correction is used to compensate for the mass-dependent transmission of the TOF mass spectrometer when performing a calibration. As only the Iodide and the PTR instruments were calibrated using a specific compound (formic acid for the Iodide and monoterpenes for the PTR instruments), we applied this correction for the medium-pressure ionization MS only. For the Amine and the Nitrate the calibration was

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inferred using the HOM molar yields, i.e., using the mass range from mass-to-charge 300 to 650 Th. As no duty cycle correction had been done in the studies from which the HOM yields were taken, we decided not to do it either. We have added a sentence to explain this choice. Lines 232-236: “For the PTR instruments and the Iodide, a duty cycle correction was applied to compensate for mass-dependent transmission due to the orthogonal extraction of the mass analyzers. The Amine and Nitrate were calibrated by scaling a wide range of mass-to-charge based on earlier studies, where duty cycle corrections had not been performed. Therefore, we did not apply such a correction for the atmospheric pressure ionization mass spectrometers.”

Line 244-250 The sensitivity of VOCUS seems to be significantly lower than the reported numbers in Krechmer et al., 2018. The sensitivity of the Vocus was indeed ~ 10 times lower compared to Krechmer et al. 2018. In this earlier study they used a much larger RF to optimize the sensitivity of the Vocus, which can lead to larger fragmentation. The aim of our measurements was to maximize the amount of compounds detected by each mass spectrometers. So rather than optimizing the sensitivity we made a compromise between fragmentation, sensitivity and mass resolving power.

We have added a sentence to explain this choice Lines 183-184: “The Vocus was operated at a higher water flow than in Krechmer et al. (2018), resulting in a decrease of the OVOC (e.g., HOM) fragmentation but also in a lower sensitivity.”

Figure 5: the y-axes in the B and D panels are covered by left ones.

This has been amended.

Section 2.3: If the ion-molecule reactions of amines and OVOCs proceed through different mechanisms, more than just adduction reaction, it is better to remind us about it.

To our knowledge and from previous work (Berndt et al., 2018), the ionization process involving amines predominately forms stable clusters with OVOC. We have added a

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sentence to mention this point. Lines 211-215: “The Amine has been shown to be sensitive towards a very wide range of OVOC, both closed shell species and peroxy radicals, from molecules with a few oxygen atoms all the way to HOM (Berndt et al., 2018). Previous work have shown that protonated amines are effective reagent ions, forming stable clusters with OVOC (Berndt et al., 2018).”

Section 2.4 The discussions in this section is very good. Is it possible to move this part to the end of the manuscript, as part of discussions from the findings of this work? We mainly reviewed current limitation. Not sure if it is useful to move this part at the end. Thoughts?

We thank the reviewer for this comment and suggestion, and agree that this is important discussion, which is rarely brought up in the literature. While it would likely receive more attention in the discussion section, we prefer to keep it where it is. Partly because most of the discussion is based on earlier studies, and would therefore greatly dilute the discussion of actual findings from this work. Partly we believe that without this section before the results, readers may have a hard time putting our results into perspective at the time they are presented.

Line 549-550 Organic nitrates usually fragment in PTR-MS instruments (including VOCUS) by losing the nitrate functional group. The authors should mention this here.

We agree with the reviewer and it is now mentioned in the manuscript. Lines 564-567: “While organonitrates have been detected before using the Iodide (Lee et al., 2016), this was the first observation that also the Vocus can detect such compounds efficiently. However, we cannot exclude that such compounds undergo fragmentation within the drift tube as commonly observed in other PTR instruments (Yuan et al., 2017).”

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