

## ***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

Received and published: 14 March 2019

Anonymous Referee #2

General comments Five different chemical ionization mass spectrometers were applied to measure simultaneously air samples from chamber experiments of  $\alpha$ -pinene oxidation under varying trace gas concentrations. The authors compare the suitability of the applied CIMS techniques for the detection of different compound classes in the investigated reaction system. The manuscript is well written and the results are clearly presented. The experimental data are of sufficient quality and the interpretation of the results is expedient. The paper provides valuable new insights in the detection

C1

of different compound classes by five different CIMS techniques. It therefore gives guidance for the selection of CIMS techniques dependent on the scientific problem to be addressed. I recommend its publication considering the following comments. We thank the reviewer for careful consideration of our manuscript.

Specific comments Chapter 2.3: While for the Nitrate- and with some limitations also for the Amine- CIMS the uncertainty of the concentration estimates are provided, this is lacking for PTRTOFMS, VOCUS and Iodide. At least for the sensitivities mentioned an uncertainty should be provided as this is an essential parameter for an instrument performance, which is stated to be evaluated. The performed calibrations should provide the possibility to derive an accuracy for those instruments.

The reviewer is correct that more discussion on uncertainties for the different instruments are warranted. However, while it is true that we can derive accuracies for the calibrated compounds, most of the reported concentrations are based on derived sensitivities (e.g., we used the sensitivity of MVK for all oxygenated monoterpene products). For the vast majority of compounds shown in the manuscript, the dominant source of uncertainty comes from the scaling of sensitivity to a certain number that was determined for another compound. Therefore, reporting a single uncertainty for an instrument is problematic.

We have now added details and discussion on the uncertainties into the manuscript to emphasize these points.

Lines 262-267: “The uncertainties for the compounds that were directly calibrated are estimated to be  $\pm 20\%$  for PTR-TOF and Vocus. For other compounds, the uncertainties are much higher due to uncertain ionization efficiencies and potential fragmentation of the compounds with unknown structures. For example, we used sensitivity of MVK for all oxygenated monoterpenes even though all those compounds may have very different fragmentation patterns, transmission rates and/or proton transfer reaction rates from each other. Therefore, we refrain from quantitative estimates of the uncertainties

C2

for these species.”

While there would be much more to say, the impact of these uncertainties is not significant for the main conclusions of the manuscript, and therefore we prefer to not go into too much detail on it there. Here, however, we wish to elaborate a bit further.

Take for example the volatile compounds measured by the PTR. These should be the easiest to calibrate out of all the measured compounds, and consequently, also the uncertainty should be the easiest to determine. The accuracy mentioned by the reviewer can be derived from the calibrations. However, other considerations are also important, such as that the standard gas manufacturer (Apel-Riemer) has promised that the reported concentrations in the standard gas mixture are within  $\pm 5\%$ . This causes directly 5% uncertainty for the concentrations of the PTR instruments. In addition, mixing the standard gas with the VOC free air (to dilute the VOC concentrations down to a few ppb) relies on the accuracy of the flow measurements themselves. Kajos et al. (2015) also noticed that sensitivities derived from different calibrations - but using exactly the same setup - seemed to be within  $\pm 10\text{-}20\%$ . This estimate includes all the uncertainties caused by the user (e.g. measuring flows slightly differently) but excludes the possible calibration error of the flow meter and uncertainty of the reported concentrations in the standard gas setup. This estimate may sound surprisingly high but it underlines that calibrating the instruments using even a gaseous standard is not straightforward. Summing all this up, we estimated that the calculated sensitivities of our PTR instruments, for the directly calibrated compounds were within  $\pm 20\%$ .

For all the other identified compounds, we needed to use a proxy for the sensitivity as discussed in the manuscript. This approach has, of course, several uncertainties. The proxy does not consider fragmentation - which can be anything from non-existent to almost 100% (e.g. many alcohols such as butanol). In addition, the proton transfer reaction rates which directly affect the sensitivity of the instrument, have large variability (e.g. Zhao et al., 2004), and the reaction rates are poorly known for many oxygenated monoterpene products. Therefore, the proper uncertainty estimates are almost impos-

C3

sible to determine for the derived sensitivities.

Page 10, lines 257f: Only data of the Iodide before December 17th was included due to decaying response. What is the reason for addressing data prior to 17th while it becomes invalid afterward. Has the sensitivity been fallen below a certain threshold or did an abrupt decay of the sensitivity occur? Please specify the reasons for the decision. As mentioned in the paper the sensitivity of the iodide abruptly changed after December 17th, so while it was possible to use the Iodide data during the first half of the campaign it appeared too ambiguous to utilize the data for the rest of our measurements. In addition, we do not know the reasons for this abrupt change so we decided to exclude these data as were not acquired in a reliable way.

There was indeed an abrupt drop in sensitivity on Dec 17, and therefore we decided to cut the data at this date. This information was now explicitly added to the text.

Lines 269-271: “Due to unknown reasons, the response of the Iodide decayed throughout the campaign, and therefore only data measured before December 17, when a stronger drop occurred, was included for the direct comparison of the non-nitrate OVOC.”

Page 11, lines 275f: Please specify what the estimate of a HOM wall loss of  $1/300\text{ s}^{-1}$  is based on.

We now added the following text to the manuscript

Lines 289-292: “This estimate is based on a rough scaling to a slightly smaller chamber (1.5 m<sup>3</sup>) with active mixing by a fan, where the loss rate was measured to be  $0.01\text{ s}^{-1}$  (Ehn et al., 2014). As our chamber is larger, and our mixing fan was only spinning at a moderate speed, we estimated the loss rates to roughly 3 times lower.”

Page 16, line 407: Please specify the threshold for an ‘abundant’ signal to be selected for further analysis.

The “abundance” related to a comparison between instruments, not to any specific

C4

threshold for further analysis. As the reviewer also mentions in a later comment, this sentence was long and complicated, and thus easily misinterpreted. We chose to remove the second half of the sentence here, as the methodology was described in more detail in a later section.

Page 17, line 449: The lack of dimers measured by VOCUS only suggests a potential limitation of the used setup/instrument parameters. It has not been shown that VOCUS is unable to measure dimers under different instrument conditions. → Replace 'instrument' by 'used setup'.

We agree with the reviewer and we have changed the sentence.

Lines 460-463: "In other words, as good correlation was seen in this mass range for nearly all compositions, the Iodide and the Vocus did not seem to be strongly impacted by the exact chemical conformation of the organic compounds. Interestingly no dimers (mass-to-charge > 300 Th) were observed with the Vocus, which suggests some potential limitation of the instrument or the used settings."

Page 18, line 462: Referring to the mass to charge ratio for ions measured by Iodide: Does that include the molecular mass of Iodide or has this been removed for comparative reasons?

As mentioned on line 430, all the mass to charge ratios used in the Figures and cited in the manuscript are reported without the reagent ion for comparative reasons.

Chapter 3.1.2: The authors speculate that the amine CIMS is capable of measuring dimers due to the formation of extremely stable amine-dimer-clusters. However, this has been observed under conditions where the reagent ion has been depleted significantly due to high trace gas loadings. Therefore the formation of dimers might be positively biased by the excess amount of uncharged monomers forming dimers by clustering with monomer-amine-clusters. Can this possibility being ruled out?

We have looked at the correlation between the most abundant monomers and dimers

C5

measured using the Amine (see Fig.1). As shown in the Figure below no obvious correlation was observed. Therefore, the possible formation of dimers from uncharged monomers clustering with cluster monomers (e.g.,  $C_{10}H_{16}O_8 + C_{10}H_{16}O_8-C_4H_{12}N^+ \rightarrow C_{20}H_{32}O_{16}-C_4H_{12}N^+$ ) can be ruled out. In addition, the good correlation with the same dimers measured by the Nitrate is extremely unlikely to be a coincidence. Finally, the depletion of reagent ions will not cause an "excess of uncharged molecules", since the fraction of any single neutral molecule becoming charged in the CI inlet is marginal.

Technical corrections Page, 11, Line 273 Change '20 p.p' to 20 % As we are referring to the difference between 50% and 70%, we believe percentage point is the correct unit, and did not make any changes.

Page,14, Line 362f; Reference for the studies using permeation sources of perfluorinated carboxylic acids is missing Two references have been added (Ehn et al., 2014; Heinritzi et al., 2016).

Page 16, Lines 404 – 408: Splitting the sentence into two would improve its readability As mentioned above, this sentence was amended.

Page 16, Line 423: change ' . . .methods, all ions were not observed. . .' to ' . . .methods, not all ions were observed. . .' It has been changed

Page 16, Line 425: use plural It has been changed

Page 23, Line 623: Should be 'Figure 7D' The correction has been made as suggested.

References Kajos, M. K., Rantala, P., Hill, M., Hellén, H., Aalto, J., Patokoski, J., Taipale, R., Hoerger, C. C., Reimann, S., Ruuskanen, T. M., Rinne, J., and Petäjä, T.: Ambient measurements of aromatic and oxidized VOCs by PTR-MS and GC-MS: intercomparison between four instruments in a boreal forest in Finland, *Atmospheric Measurement Techniques*, 8, 4453–4473, 2015.

Zhao, J. and R. Zhang: Proton transfer reaction rate constants between hydronium ion ( $H_3O^+$ ) and volatile organic compounds. *Atmospheric Environment*, 38, 2177–2185,

C6

C7

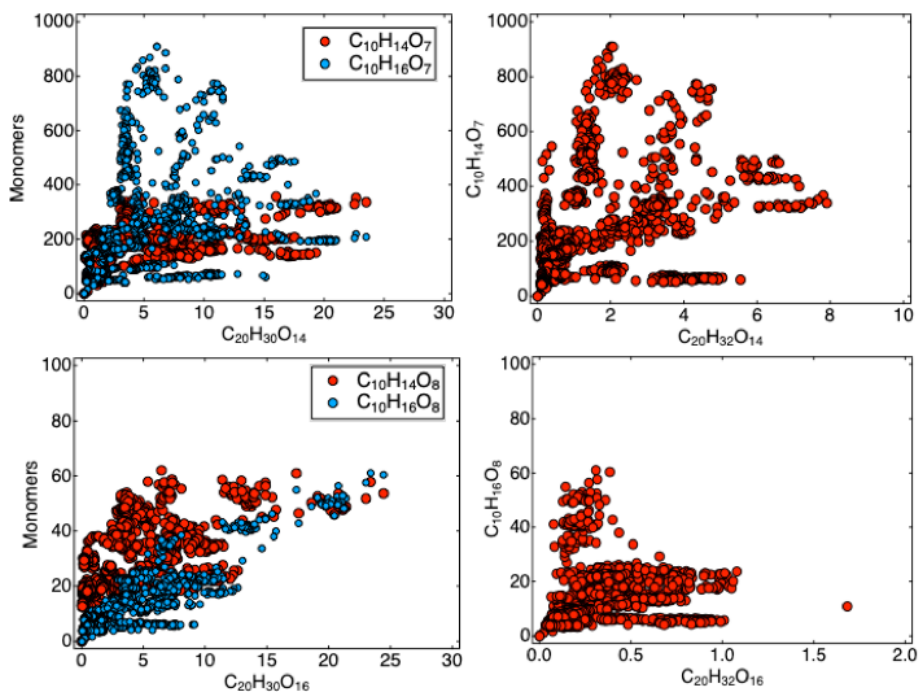


Fig. 1.

C8