

## ***Interactive comment on “A compact PTR-ToF-MS instrument for airborne measurements of VOCs at high spatio-temporal resolution” by M. Müller et al.***

**Anonymous Referee #2**

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The authors present a valuable development and first-time airborne deployment of PTR-ToF-MS. This interesting methodology paper is further complemented by initial results from the instrument's deployment during the NASA DISCOVER AQ campaign.

A major advantage of the presented instrument seems to be in its ability to measure the entire VOC spectrum almost instantaneously without the need for preselecting the  $m/z$  as is the case for the QMS systems. The compact ToF detector does not have as high mass resolution as some other ToF detectors available on the market (e.g. ToF 8000), but the authors make it clear in the text and they claim that this resolution is sufficient for separating ions of the same nominal mass but different exact masses. This has been demonstrated for several example VOC pairs (e.g. isoprene and furan) all in the relatively low mass range.

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While the authors find clear advantages of presented PTR-(compact)ToF-MS relative to PTR-QMS, such as improved mass resolution, I think the latter instrument still has certain advantages for airborne research (e.g. high sensitivity, relatively more compact dimensions/weight). This can likely change in the future along with the ToF detectors and PTR front ends becoming better and better. Overall, I would have no hesitation to recommend this novel paper, and would like to offer my relatively minor suggestions which hopefully can be considered by the authors before the publication in AMT.

### **General**

1) There are not too many references in this paper. I am specifically missing links to other recent airborne studies (e.g. in California) which could provide a better context for the current airborne VOC research.

2) In this compact methods paper, I am also missing a data inter-comparison with other instruments. The authors nicely demonstrate the in-flight calibration curves, detection limits, etc., but it would greatly add to the value of the paper if the authors actually compared the data to those from a different instrument (which may be particularly important to substantiate more strongly the results from Figure 10, in particular ammonia – see comment below).

3) Because the methods for ammonia are not provided, I am somewhat unconvinced about ammonia results included to VOC results and perhaps they are diluting the otherwise coherent message. It is well known that measurements of ammonia are very challenging due to losses in the inlet and there are more dedicated instruments to measurements of ammonia (e.g. von Bobrutzki et al., 2010). PTR-MS is typically used in  $O_2^+$  ionization mode to measure ammonia (e.g. Norman et al., 2007), while I suspect the authors operated exclusively in  $H_3O^+$  mode. Is this correct? If so was the residual  $O_2^+$  sufficiently high and stable (e.g. when humidity changed) to ensure efficient ammonia detection? Was the signal for ammonia normalized in the same way as VOC ions resulting from  $H_3O^+$  chemistry? Furthermore, it is not clear to the reader which

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m/z authors attributed to ammonia as it is not included in Table 1.

4) While the authors did an excellent job in advertising instrumental advantages, I wonder if it would be worth balance a little with some of its limitations (challenges, future direction).

Specific

5) Title. The word “compact” might suggest the instrument is compact, while it probably refers here to the compact ToF detector and not to the dimensions or weight of the instrument. Can you include (e.g. in Sect. 2) the info on instrument dimensions and weight?

6) The mass resolution looks much better than nominal but certainly not as good as in ToF 8000 detectors. As  $\Delta m$  degrades with increasing m/z, this may be particularly relevant for measurements of larger m/z and can make separation of heavier compounds (e.g. >100 Th) difficult. It might be worth making more clear in the text how mass resolving power and resolution relate to m/z and where exactly in the m/z range the limitations start to appear.

7) P5534 L4 “The new instrument resolves isobaric ions” is not strictly true, because the instrument cannot resolve the species of exactly the same mass (isobaric). Consider saying something like: “...can resolve compounds of the same nominal mass but different exact mass...”

8) P5534 L5-7 “...records full mass spectra at 1 Hz and thus overcomes some of the major analytical deficiencies of quadrupole-MS based airborne instruments.”. Consider replacing with a more positive expression (e.g. “...simultaneously at 1 Hz and thus is a major step forward from quadrupole-based instruments which had to sequentially analyze consecutive m/z.”

9) P5534 L8 It should probably be “total monoterpenes” as  $\alpha$ -pinene has the same exact mass as other monoterpenes, so cannot be separated using the PTR-ToF-MS

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(at least at a constant E/N as typically used).

10) P5534 L7 “detection limits...making the instrument well suited for fast measurements in the continental boundary layer”. I suggest to clarify “...measurements of abundant VOCs in the continental boundary layer”.

11) P5534 L22 VOC mixing ratios range from pptV... I would say VOC range from less than pptV ...

12) P5535 L16 Consider providing a context here to other recent airborne deployments (e.g. INTEX, MILAGRO, CALNEX, CABERNET) which took place after the review by de Gouw and Warneke (2007).

13) P5538 L18 “heated silanized stainless steel line”. Did you notice any memory effects or problems for methanol? Why was this material chosen for VOCs/ammonia?

14) P5539 L12-15 “For in-flight calibration, the flow of VOC-free air is spiked with ~5 ppbV of the target VOCs. Spiking is also carried out at different altitudes to characterize any humidity dependence of instrumental response factors. We use a certified 11-15 component VOC mixture...”. How long did it take to equilibrate post these 5-ppb spikes before ambient signal was measured/reported? Did these spikes raise the detection limits for the sticky compounds?

15) P5539 L22 “A three-way valve”. What kind of valve, what materials?

16) P5540 L10-11 “...signals (m/z 21.022, m/z 39.033 and m/z 55.039) are used for mass axis calibration and reference peak shape determination.” Was it not possible to use any intrinsic heavy masses to improve the accuracy in the higher mass region (e.g. >100 Th)?

17) P5442 L1-3 “These results demonstrate that two isobaric peaks at m/z 33 are well resolved and accurately positioned ( $\Delta m \leq 1.0$  mDa) even with a relatively low mass resolving power of 900.” The  $\Delta m$  for methanol seems quite good (1 mDa) but gets somewhat worse for acetone (4 mDa), isoprene (5 mDa), and as one goes along the

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m/z range (Table 1). This is still impressive relative to nominal and should be sufficient for separating the ions differing in oxygen number, at least in the low to medium mass range. I wonder though if the signal abundance can affect the accuracy of the peak positioning of a partially merged peak?

18) P5542 L28-29 "...which identified furan as the dominating species detected at m/z 69". Needs to make it clear that this refers to biomass burning.

19) Figure 8. I can see the peak at m/z 124 and I know at least one PTR-ToF instrument where this peak was intrinsic. Could it be intrinsic also here? If so this peak probably should be omitted from the figure, but maybe could be useful for aligning the mass scale?

20) Figure 9. Top. Would it be useful to zoom in to the area with high toluene mixing ratio (~2 ppbv) (maybe as an inset)?

21) Figure 10. Apart from methanol which has been thoroughly discussed, neither acetic acid, formic acid nor ammonia are discussed, or mentioned in Table 1, or seem to have been present in the calibration standard, so it is unclear how the concentrations were derived and what is the uncertainty. See also earlier comment #3 for ammonia. Perhaps vertical profiles of other VOCs (e.g. from Table 1) could be more relevant to present as examples here or would it be possible to add an intercomparison figure?

22) Conclusions. Could be expanded to include most important points from the study. For example, consider highlighting that this was the first airborne deployment of a PTR-ToF instrument.

#### References:

von Bobruzki, K., Braban, C. F., Famulari, D., Jones, S. K., Blackall, T., Smith, T. E. L., Blom, M., Coe, H., Gallagher, M., Ghalaieny, M., McGillen, M. R., Percival, C. J., Whitehead, J. D., Ellis, R., Murphy, J., Mohacsi, A., Pogany, A., Junninen, H., Rantanen, S., Sutton, M. A., and Nemitz, E.: Field inter-comparison of eleven atmospheric

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