

Atmos. Meas. Tech. Discuss., author comment AC1 https://doi.org/10.5194/amt-2022-168-AC1, 2022 © Author(s) 2022. This work is distributed under the Creative Commons Attribution 4.0 License.

### **Reply on RC1**

Alexander Håland et al.

Author comment on "On the development of a new prototype PTR-ToF-MS instrument and its application to the detection of atmospheric amines" by Alexander Håland et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-168-AC1, 2022

We thank referee #1 for having carefully read our manuscript and for making very valuable comments and suggestions. Here is how these were addressed:

For measuring sticky compounds present at low mixing ratios such as amines, instrument and inlet background/zero determination is critically important. In order to properly judge the prototype instrument, further information on both instrument and inlet background are required. For instance, how frequently and for what length of time were zeros performed for the ambient measurements? How reproducible/stable were the backgrounds? Did relative humidity changes influence the background (particularly the inlet background)? Seeing a time series showing both ambient and background data would also support the claims about the short response time and the reduction in memory effects. Although the paper focuses on the instrument and not the inlet per se, information on the inlet background and response is necessary for the reader to critically evaluate the ambient measurements.

#1: We fully agree that background/zero determination is a critically important aspect. In the revised manuscript, we describe how frequently and for what time length zeros were performed (lines 145-146, 175-176). We also add two figures in the Supplement showing the low and stable instrumental backgrounds for DMA, TMA and AMP. When reanalyzing the data, we noticed that the variable MMA background (measured at m/z 32.049) correlates with the  $O_2^+$  signal (measured at m/z 31.989). It turned out that also most of the m/z 32.049 signal variations in ambient air were caused by variations in the  $O_2^+$  signal. We thus have to withdraw the MMA data in the revised version of the manuscript.

## *Given that this is an instrument paper, detection limits, precision, and accuracy should be reported.*

#2: Yes, this was also a major omittance. In the revised manuscript, we are reporting all these figures of merit (lines 160-161, 166-167, 202, 228, 230, 245, 259).

The time resolution of the measurements should be more clearly presented particularly for the data presented in figures 5, 7, and 8. Without this information, it is challenging for the reader to adequately judge instrument performance.

#3: The time resolution is now reported in the respective figure captions and in the main text.

Several steps were taken to improve response time (increased flow through the flow reactor heated lines, NH<sub>3</sub> addition). If available, I think it would be beneficial to include information on the relative impacts of these different steps. Steps such as heating lines to 100 degrees Celsius can be challenging in certain deployments and NH<sub>3</sub> adds additional complexity (and corrosion concerns). It would be beneficial to the community to understand which practices are the most critical for response time.

#4: Increasing the flow through the drift tube was the most critical step. This is now further emphasized in the manuscript: "Our key strategy for reducing the instrumental time response was to maximize the flow through the low-pressure flow reactor. A dry multi-stage Roots pump (ACP40; Pfeiffer Vacuum, Asslar, Germany) pumps up to 0.80 slpm (standard liters per minute) through the FIMR. For the measurements presented herein, we set the flow rate to 0.55 slpm, which is a factor 5 higher than in commercial VOCUS instruments (Krechmer et al., 2018; Wang et al., 2020). We observed that increasing the reactor flow from 0.05 to 0.50 slpm reduced the  $1/e^2$  decay time of a 20 pptv trimethylamine (TMA) signal from ~60 to ~5 seconds." The other two measures (heating the lines, addition of NH<sub>3</sub>) were unfortunately not investigated in a systematic way and were implemented based on our previous experience with measuring amines in atmosphere simulation chambers.

# *I ask the authors to consider adding examples of ambient mass spectra, particularly around the ions of interest, for the NH4+ and H3O+ modes. This would provide justification for the claims about simplifying interpretation.*

#6: We are withdrawing the claim about simplifying interpretation, at least when small alkylamines are the target compounds. While the overall mass spectrum becomes indeed simpler in the  $NH_4^+$  mode, protonated DMA and TMA are easy to detect in a medium resolution mass spectrum both in the  $H_3O^+$  and in the  $NH_4^+$  mode. Our original assumption was that a lower  $O_2^+$  background in the  $NH_4^+$  mode would improve the detection of MMA, but a more careful reanalysis of the data revealed that this is not the case. Please also see comments #1 and #10 (in reply on RC1) for more details.

#### Given that the applications described are amine measurements, the introduction should include a brief summary of the various techniques that have been used for amines rather than just focusing on comparisons to the VOCUS. Specific advantages relative to those measurements should also be detailed.

#7: The paper is conceived as a description of new PTR-MS prototype instrument, and the introduction puts it into that context. We feel that an additional paragraph on different amine detection technologies. would disrupt the reading flow and not really fit into the introduction. We do however agree that additional direct injection CIMS methods should be mentioned and have thus included one extra sentence and several references: "Direct injection CIMS is thus the method of choice for measuring pptv levels amines in the atmosphere in real time, and a series of instruments have recently been developed for measuring amines (Sellegri et al., 2005; Hanson et al., 2011; Yu et al., 2012; You et al., 2014; Zheng et al., 2015; Yao et al., 2016; Wang et al., 2020; Pfeifer et al., 2020; Lee 2022)."

### Please fix the section numbering (there are two section 2.2)

#8: Done. Thanks for spotting this.