

Atmos. Meas. Tech. Discuss., author comment AC2
<https://doi.org/10.5194/amt-2022-168-AC2>, 2022
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Reply on RC2

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-AC2>, 2022

We also thank referee #2 for having carefully read our manuscript and for her/his valuable comments and suggestions. Here is how we addressed these:

In the introduction from around line 51-65 there is a verbal comparison of the HCGD ion source to the VOCUS source. There are several lines here that suggest potential issues with the VOCUS source, that are not supported by data, meant to indicate that these are issues with the VOCUS ion source. It seems inappropriate to criticize the VOCUS for theoretical issues which are not investigated within this work, nor are necessary to understand this manuscript. This seems inappropriate and I believe this section should be removed.

#9: In our opinion, it is appropriate to mention potential problems of an existing instrument in the introduction of a chemical-analytical paper. We provide solid scientific arguments, explicitly state that these are only potential problems and do not use discrediting words. In our opinion, it should be allowed to raise concerns over an existing ion source design and make the scientific community aware of these. However, we do not insist on including this paragraph. If the Editor also thinks this is inappropriate, we simply remove these statements.

In general, this paper feels like it is lacking in the detail necessary to make it a strong addition to instrumental papers on the NH₄⁺ techniques that are being used. Perhaps I missed it on my read throughs, but it doesn't seem like the authors even give details on what ion source fuel was used to generate NH₄⁺, was it a water solution containing NH₃? In terms of the ion generation more details on how clean the spectra are with respect to potential primary ions is needed, how effectively do the conditions identified/used reduce the NH₃-NH₄⁺ or NH₃-H₂O⁺ ions which may lead to alternative products that would complicate the spectra. Showing a spectrum and the relative abundance of these ions would be beneficial. Additionally, for any calibrants that were measured perhaps the authors could give a comprehensive list of where else in the spectra ions were observed. Is there any fragmentation occurring, or unintended products observed. Do you see both adduct and proton transfer products.

#10: This paper is actually not intended to be "a strong addition to instrumental papers on the NH₄⁺ techniques". The focus is the new instrumental design, which combines an HCGD ion source with an FIMR. We used this new instrument for measuring amines, which

can be achieved by either operating in the H_3O^+ or NH_4^+ mode. We have removed the paragraphs/sentences that suggest the latter is more suitable for measuring small alkylamines.

The source gas in the ammonia mode is described in lines 156 and 157 of the original manuscript: $F_{\text{source}} = 6 \text{ sccm } 1\text{-}3\% \text{ NH}_3 \text{ in } \text{N}_2$. In the revised manuscript, we provide a slightly modified and hopefully clearer description of the operational settings of the ion source (lines 148-151).

In the revised manuscript, we also list all additional ions with a relative abundance $>1\%$ of NH_4^+ (lines 150-151). We do not think it is necessary to add an extra figure for conveying this information.

We also explicitly state that $[\text{M-H}]^+$ ions are the only additional product ions observed for the investigated amines (lines 196-197).

Without an actual comparison to a VOCUS ion source it is difficult to understand if this HCGD source coupled to the FIMR TOF is indeed an advantage over the commercially available VOCUS package. Do the authors have any data that can serve as a point of comparison?

#11: Unfortunately, we do not own a commercial VOCUS instrument and are thus not able to make such a comparison. We also want to emphasize that this paper should not be interpreted in a competitive context. We do not want to present a "product" that is better than existing commercial analyzers; we simply present a prototype instrument that is new and different.

It is clear that this instrument functions well, but the package is not commercially available and as far as I understand you cannot purchase a VOCUS with a HCGD, nor are the design plans for the HCGD publicly available to my knowledge, so I am not sure how useful this work is if the instrument is a specialized one-of-a-kind instrument. Am I missing something, and this would in fact be a system that could be reproduced easily or purchased?

#12: This is a comment we do not understand. The scientific literature (and in particular AMT) is full of descriptions of "specialized one-of-a-kind" instruments, i.e. instrument prototypes that are only used by one research group. Such papers mainly serve as a reference for future publications, in which the data collected with these new analyzers are presented. Another motivation is that other groups could build the same or a similar instrument. Again, there is no commercial motivation behind our work.

There are clearly data gaps in the time series shown in figure 5 which are possibly instrument zeros, it would be helpful to see the zero data in these figures, or at least an inset of data showing the zeroing. The same is desired for figures 7 and 8, where without the zeros it is impossible to determine if these features are driven by changes in instrument backgrounds or real ambient observations.

#13: We now provide two additional figures in the Supplement that include the zero data.

In line 245 the authors point to the potential interpretation of 1 ppt signal variation on a 1-minute signal. Without knowledge of the instrumental detection limits, which are currently missing from this work it is unclear if you can even interpret that information. It is possible that the 1ppt variations are simply due to unstable instrument conditions. Showing background periods associated with that data and the experimentally determined detection limits during that

measurement period is necessary to imply observations are interpretable on that level.

#14: This is correct. We now include a statement on the detection limit and give an additional figure in the Supplement showing the variability of the instrumental background. "The instrumental background was low and stable (0.6 ± 0.2 pptV) throughout the measurement period (see Figure S2), which resulted in a detection limit (3s, 5-min signal integration) of 0.5 pptV for AMP."

Specific comments:

- ***Line 31, rewrite to read "Because of the presence of an electrostatic field..."***
- ***Line 45, ions is are sampled***
- ***Line 67, the word exemplary is used here to describe laboratory and field data but it is nonquantitative and should be removed.***

#15: We have adopted two of the suggested changes. We think that "...fraction of the ions is sampled" is correct.