

Interactive comment on “Measuring acetic and formic acid by proton transfer reaction-mass spectrometry: sensitivity, humidity dependence, and quantifying interferences” by M. Baasandorj et al.

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We thank the referees for their valuable time and constructive comments. We addressed each of the reviewers' comments and made minor revisions to the manuscript as outlined below.

Referee #1

Referee comment: page 10889, section 2.1: Although the authors point to another

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manuscript for details on the inlet, due to the discussion here about memory effects it is necessary to give the reader a few details on the inlet used (e.g. tubing size, flow rates, length) such that a residence time can be calculated easily.

Author reply: As requested also by another referee (# 2), the section 2.1 now has more details (generation type, drift tube length) on this particular instrument. Page 10889 line 19: inserted “The inlet system is designed to sub-sample a flow of ~1000 sccm through 3 m of 1/2” OD PFA tubing followed by 1 m of 1/4” OD PFA tubing. Of this, ~35 sccm is sent to the PTR-MS via 1 m of 1/8” PFA tubing.”

Referee comment: page 10895, line 21: i believe you should add the words “lower degree of” before fragmentation.

Author reply: page 10895 line 21: inserted “lower degree of” before fragmentation

Referee comment: page 10899, line 15: I do not understand how the authors can state that PAA will go mostly to AA-H⁺ if the standard available itself contain AA. It seems to me that as these are inseparable then no conclusions could be made.

Author reply: It is true that the ion at m/z 61 resulting from AA-H⁺ and PAA-H⁺ are inseparable. However the dependence of the product ion distribution on E/N can shed light on whether the ion signal at m/z 61 is dominated by a fragment ion of PAA-H⁺ or a parent ion of acetic acid. We observed an increase in the abundance of product ion at m/z 61 and a decrease in PAA-H⁺ at m/z 77 with increasing E/N values, which is consistent with the fragmentation of PAA-H⁺. In contrast, with pure AA standard, the molecular AA-H⁺ ion decreases with increasing E/N. As discussed in the manuscript, Spanel et al. 2003 also observed a major product ion at m/z 61 and attributed it to AA-H⁺. Obviously there is an uncertainty about the exact mechanism involved. But the most likely pathway for the formation of AA-H⁺ is via elimination of the -OH group from PAA-H⁺ (as the bond between oxygen and peroxidic OH is weaker than the carbonyl bond) followed by H atom transfer.

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Referee comment: page 10900, line 21: The authors should clarify that the reason they did not quantify DME is due to the problems with quantifying the standard not in using a catalyst to acquire an instrumental background as is often used in PTRMS.

Author reply: changed “a catalytic converter” to “a high temperature”

Referee comment: page 10901, line 25: put m/z in front of 79 for consistency.

Author reply: done

Referee comment: page 10903, line 20: Again how can you quantify the retention of PAA if it is detected mostly as AA-H⁺ and the PAA standard contains AA?

Author reply: Even though the abundance of the parent ion (at m/z 77) is low, we were still able to use the change in signal to determine if PAA is retained completely.

Referee comment: page 10904, line 6: What was your typical H₃O⁺:H₂O-H₃O⁺ ratio since we are thinking in terms of your previous figures.

Author reply: Figure 4 shows the range of IH₂O-H₃O⁺/IH₃O⁺ ratio during the field campaign. A typical value was ~ 0.06.

Referee comment: page 10907, line 4: I believe this sentence is missing a word and needs to be rewritten.

Author reply: replaced in line 4, “and as with AA and glycolaldehyde, they were highest” instead of “and as with AA and glycolaldehyde were highest”

Referee comment: Figure 5: I would suggest moving the RH% legend out of the graph panel and into the general open space to make it more visible. Same for Figure 6.

Author reply: Thanks for the suggestion. We prefer to keep this figure as-is. We will ensure that when figures are converted to their final size for AMT, all text, legends, etc are clear and legible.

Referee comment: Figure 10: There is so little ambient data shown in Figure 10. As

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a reader I would like to see more instances of this especially with additional ambient structure that you discuss in the manuscript. The data here looks like it could be laboratory standards. In putting this into practice it would benefit the reader to see more continuous data here.

Author reply: The figure does in fact show ambient data: the black points are ambient air sampled via the acid trap). The grey points show the corresponding trap background measurements. We find that adding more data to the figure makes it made it too busy and confusing to interpret. Thus we have kept it as-is.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 10883, 2014.

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