

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 #4

Referee comment: P10889 L22-P10890 L11: The authors discuss memory effects

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due to adsorption of FA and AA inside the sampling inlet. Please indicate the length of the sampling line and the sampling flow rate. Were the tests repeated under different relative humidity conditions? Does water adsorption on the Teflon surfaces lead to different memory effects?

Author reply: We tested the disappearance for the acids under different humidity conditions with heated lines and found similar results. It is not certain how the water adsorption on the inlet surfaces would affect the loss of AA and FA, but in our case, the use of heated lines not only improves the efficiency of acid delivery but also reduces the equilibration time for change in water vapor concentration. So water adsorption in our inlet system is minimized.

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: The authors indicate that the ‘disappearance time’ for AA and FA decreased to 4 and 8 minutes, respectively, using a heated inlet. What was it at ambient temperature? Could the authors comment on the fastest time resolution that could be achieved based on the observed memory effects?

Author reply: As indicated earlier in that same paragraph, the disappearance times were initially 20-25 minutes when not using a heated inlet.

Page 10890 line 11: inserted “(e-folding times of less than 20 s and 40 s)” before “shorter than has been reported”

Referee comment: P10891 L5-7: “CO₂ mixing ratios are generally varied ...”. Should we read “The changes in CO₂ mixing ratios . . .”?

Author reply: P10891 L13-14: Yes, the reviewer’s interpretation is correct. We believe this statement is sufficiently clear as-is.

Referee comment: P10891: Were permeation rates derived for each permeation tube

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from the CO₂ measurements performed during calibration experiments? If so, did the authors try to compare these determinations to permeation rates derived from gravimetric measurements?

Author reply: We examined the permeation rates to ensure their stability, and did not compare these with gravimetric measurements since the CO₂ calibration already enables an absolute quantification.

Referee comment: P10893 L22-25: "Due to small (< 10 %) calibration offsets under laboratory vs. field conditions. . .". Could the authors comment on this observation? Where does this offset come from? What is the impact for field measurements?

Author reply: The environmental conditions in the field were very different than the controlled lab environment. Several factors, including high ambient temperature and humidity (often ~ 100 °F and 100 % RH) in St. Louis, as well as fluctuation in temperature and ventilation issues inside a small trailer, affected the performance of the instrument in the field and led to slightly lower sensitivity.

Referee comment: P10893 L25-26: "Figure 6 shows the corresponding relative yields of major product ions for each analyte". How were the yields calculated? Was it from a ratio of measured signals or did the authors take into account the ion transmission at each mass of interest?

Author reply: The yield was derived from the ratio of measured signal over the total signal of all major ion products, and we have now clarified this in the paper. Page 10894 L26: inserted "(i.e. the ratio of the measured signal to the total signal from all major product ions)." after "relative yields of major product ions for each analyte"

Referee comment: P10897 L1: ". . .dissociation of AA-H⁺ via interaction with water molecules. . ." and L14-15: ". . .fragmentation of FA-H⁺ is enhanced by the presence of water molecules at high E/N". Do the authors have ideas about the molecular processes underlying these observations?

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Author reply: We speculate that these processes occur via a formation of a complex bound by dipole-dipole interaction between an -OH group of the protonated compounds (AA, FA..) and H₂O, which subsequently dissociates upon collision to eliminate the -OH group.

Referee comment: P10902 L9-20: Please provide more details about the trapping system and the laboratory conditions when it was tested (adsorbent mesh, trap temperature, sample humidity. . .). Could changing ambient humidity levels have an impact on the trap efficiency? Did the authors check that the trap was still removing more than 99% of each acid at RH values higher than 80-90%?

Author reply: Page10902 line 15: replaced "(Restek Corp.)" with "(mesh 60/80; Restek Corp.)". Page10902 line 15: inserted "kept at ambient temperature and" before "installed immediately upstream..". Our laboratory tests showed that the water vapor is not retained in the trap and the trap performance is not influenced significantly by high humidity or changes in humidity.

Referee comment: Table 2: What is the use of R8a, R11a, and R14a?

Author reply: These are meant to show formation of an energized adduct that can either dissociate or get stabilized.

Referee comment: Figure 3: I agree with the second reviewer that forcing the calibration line by zero is not a good practice. Could the authors comment on the significance of the intercepts when the lines are not forced to zero?

Author reply: We agree. The intercept values are small <15 ncps, less than 4 % of the minimum normalized signal in y axis of Figure 3. Page 10921: The lines are not forced to go through zero in Figure 3. Page 10916: The corresponding sensitivity values are updated in Table 1.

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

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