

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.

Anonymous Referee #4

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Review of Baasandorj et al., AMTD, 7, 10883-10930, 2014

This manuscript reports laboratory characterizations and field testing of a PTR-MS instrument to assess the performances of this technique for measuring formic and acetic acids. The investigations of the PTR-MS sensitivity and its dependence on humidity are performed thoroughly and provide important details for other PTR-MS users. In addition, the authors propose an interesting method to quantify measurement interferences, which can then be subtracted from ambient measurements of these 2 carboxylic

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acids. Overall, this study indicates that quantitative measurements of formic and acetic acids are feasible using PTR-MS.

This manuscript is well structured, clear and concise, and will be of interest for the atmospheric community. I therefore recommend publication in AMT after the authors address the following comments:

As stressed out by Reviewer #2, please indicate detection limits and précisions.

Minor comments:

P10889 L22-P10890 L11: The authors discuss memory effects 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?

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?

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

P10891: Were permeation rates derived for each permeation tube 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?

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?

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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?

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?

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%?

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

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?

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