Atmos. Meas. Tech. Discuss., 7, C4700–C4704, 2015
www.atmos-meas-tech-discuss.net/7/C4700/2015/

Atmospheric Measurement Techniques Discussions

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.

M. Baasandorj et al.

mbaasand@umn.edu

Received and published: 22 January 2015

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 comment: Page 10889 Lines 5-10, Section 2.1 PTR-MS and Inlet system Writing that the system used in this study is the one described by Lindinger et al. (1998) and the review by de Gouw and Warneke (2007) is probably too broad. Ionicon has

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

iterated the basic PTRMS design several times over the years with both incremental and major changes. Perhaps fearing competition, the changes have not been well documented or publicized. Several points that come immediately to mind are the drift tube materials and geometry, the conductance of the intermediate vacuum skimmer and orifice on the high sensitivity model, and the quadrupole used. The overall trend has been toward better RH+ transmittance, higher H3O+ densities, lower H3O+(H2O)/H3O+ ratios, with better response times and lower background signals. (Ionicon describes their current model as 4th generation.) Providing the reader with more details, such as the year delivered, will help to chronologically place the specific instrument used. That the authors achieve a primary ion signal of 1Å∼10ˆ9 cps suggests that they are working with a very recent system.

There are aspects of this study that would be hard to reproduce on the early PTRMS instruments due to their high H3O+(H2O) production and other limitations (Early PTR-MS users sometimes run with a higher ion source water flow rate, 8-14 sccm, to increase the water vapor concentration in the drift tube, so that the relative change in H3O+(H2O)/H3O+ with RH would be very small. This is something that's hard to do with newer systems). There are also some book keeping notes that should be present in the manuscript for completeness: It would be informative to know the ion source water flow rate the authors used in the lab study, the drift tube temperature, the nominal drift tube length (9.6 or 10 cm), and the integration or averaging times used in the lab study.

Author reply: Page 10889 Line 6: replaced "(HS-PTR-MS)" with "(HS-PTR-MS; manufactured 2008, generation 3 type)" Page 10889 Line 13: inserted "(9.2 cm long)" after "drift tube". Page 10889 Line 21: Inserted "The water flow rate was maintained at 6.5 sccm, and averaging times for the subject species were varied between 2 - 10 s for the results presented here".

Referee comment: Page 10890 Lines 10-15, Section 2.3 Permeation based VOC calibration system and validation: Here a catalytic converter is listed as running at 350 C,

AMTD
7, C4700–C4704, 2015

while above a similar one is listed as 400 C. Check this for correctness. Was the converter checked for conversion efficiency? Did it matter? These particular converters have some reputation for not yielding total VOC reduction (around 80-90%). However, when measuring calibration gas at 10's of ppbv (on the PTR-MS), this is hardly an issue.

Author reply: We have two catalytic converters. There is a heatbox with catalytic converter (kept for 400 °C) for determining the instrument background while the second one is used in the permeation based calibration system for conversion of VOCs to CO2 and is kept at 350 °C. The former is kept at higher temperature to ensure complete conversion of the larger sampling flow (> 1 LPM vs. 10 – 15 sccm of cal. flow). We validated the complete conversion efficiency of the catalytic converter in the calibration system.

Referee comment: Page 10890 Lines 10-15, Section 2.3 Permeation based VOC calibration system and validation: Somewhere it would be nice to see your estimated limits of detection for acetic acid, formic acid, and perhaps the other compounds you test.

Author reply: We added a new column to Table 1 listing the detection limits for this work and previous studies.

Referee comment: Page 10904 Lines 5, Section 3 Deployment and performance in the field: Is this really water flow to the drift tube or to the ion source? If it's to the drift tube, outline how the branching between the skimmers and the pinhole were determined.

Author reply: This flow is going through the ion source. Replaced "the drift tube" with "the ion source"

Referee comment: Table 1: -Haase et al (2012) report the ratio of m/z 21 to m/z 37 on Table 2 of their manuscript. - It might be useful to note in the caption or as footnote that you're restricting your review of response factors to high E/N (>100 Td or so) -This would be a fine place to list your detection limits.

AMTD

7, C4700–C4704, 2015

Author reply: Agreed. A new footnote “1 Sensitivities are compared for E/N > 100 Td” is added.

Referee comment: Figure 3: -Is the fit line through zero a result of background subtraction or forcing the linear regression through zero? Forcing the function is not a good practice since it assumes linearity which may not actually exist. The acetic acid and formic acid data for RH of 11% seems to have a lot of variance in it while the measurements at higher RH are more uniform, laying very close to the fit line. Are the higher RHs averaged in some way? Why are they so different (less numerous and less variant) than the 11%?

Author reply: The fits forced to go through zero agree with those not forced to zero within 4 %. The data for RH of 11% (a representative lab RH) seem more scattered because of the larger number of points and reflect variability of the sensitivity over an extended period of time (several months/a year) and a small fluctuation of RH. On the other hand, the other curves were all obtained within 1-2 days for each RH value. Page 10921: Figure 3 is updated so the lines are not forced to go through zero. Page 10916: The corresponding sensitivity values are updated in Table 1.

Referee comment: Figure 5: These graphs are great and add a lot of information in a small space. The vertical axis of the plots should show the entire range of the data. Instead, values below 100 E/N are clipped for most of these plots, so the high values at 86 Td are not visible. Is there enough variance at each data point to include error bars?

Author reply: These plots already contain a lot of information. If we show the entire range of data, it is hard to see the trends of those at the lower range. The goal of the plot is to show the distribution of the ion products and their trend. Also, we found that including the error bars made the plots far too busy so we kept them as is.

Referee comment: Figure 10: Including uncertainty in the data points here would also demonstrate when the signals were modified by the acid trap or not (though at 40 ncps,

AMTD

7, C4700–C4704, 2015

those may be on the scale of the data points).

Author reply: As discussed above, it makes the plot too busy.

Referee comment: Figures 11 and 12: Consider making these plots wider and taller to use up more of the page (i.e. make them 17 cm or so wide). They are so small as rendered that it is very hard to really see what is going on.

Author reply: Thanks for the suggestions. Our original plots are big occupying the entire page. We will ensure that when figures are converted to their final size for AMT that all text, legends, etc are clear and legible.

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