Review of

Measuring acetic and formic acid by proton transfer reaction-mass spectrometry: sensitivity, humidity dependence, and quantifying interferences

Submitted By Baasandorj et al.

Summary

This manuscript provides the most detailed discussion of measurements of acetic and formic acids by proton transfer reaction mass spectrometry (PTR-MS) produced to date. The authors discuss the relationship between PTR-MS drift tube field strength (E/N) and humidity with response and fragmentation both compounds, as well as a host of other compound (peroxyacetic acid, glycoaldehyde, dimethyl ether, ethanol, and propanols). With respect to the empirical relationships between humidity, fragmentation, and field strength, this paper particularly exhaustive and informative, and the authors are commended on the quality of their work. The paper also presents some illustrative field data using a novel acid scrubbing approach which shows that the dominant ions at m/z 61 and m/z 47 are acetic acid and formic acid, with periodic excursions caused by other compounds. Overall this paper is a very strong contribution to both the PTR-MS methods literature, and is of interest to those in community looking for affordable measurements of acetic and formic acids.

Generally the paper is very clearly written, and I think it should be accepted Published into ACP. There are a few minor points that the authors should consider addressing before final submission.

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 iterated the basic PTR-MS 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 H_3O^+ densities, lower $H_3O^+(H_2O)/H_3O^+$ 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 1×10^9 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 PTR-MS instruments due to their high $H_3O^+(H_2O)$ 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 $H_3O^+(H_2O)/H_3O^+$ 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.

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, 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.

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.

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.

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.

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%?

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?

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

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.

References:

de Gouw, J., and Warneke, C.: Measurements of Volatile Organic Compounds in the Earth's Atmosphere Using Proton-Transfer-Reaction Mass Spectrometry, Mass Spectrom. Rev., 26, 223-257, doi: 10.1002/mas.20119, 2007.

Haase, K. B., Keene, W. C., Pszenny, A. A. P., Mayne, H. R., Talbot, R. W., and Sive, B. C.: Calibration and intercomparison of acetic acid measurements using proton-transfer-reaction mass spectrometry (PTR-MS), Atmos. Meas. Tech., 5, 2739-2750, doi: 10.5194/amt-5-2739-2012, 2012.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research, Int. J. Mass Spectrom. Ion Processes, 173, 191-241, 1998.