

Interactive comment on “Calibration and intercomparison of acetic acid measurements using proton transfer reaction mass spectrometry (PTR-MS)” by K. B. Haase et al.

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Thank you very much for reading our manuscript and sharing your thoughts. Our responses to your comments are shared inline below.

1: The range of calibration factors (7-10.9) is mostly due to the relative fractions at m43 and m61. When taking into account the signals at both masses the calibration factors fall into a much narrower range. This should be pointed out. The remaining differences are probably due to differences in the MS transmission characteristics. The discussion is limited to reporting calibration factors. How-

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ever it would be interesting to explore if this is in agreement with the reaction rate constant and the kinetics in the drift tube! This could be done, for example, according to the method described by Holzinger et al. (Atmos. Chem. Phys., 10, 2257–2267, 2010). They also show a transmission curve which can be used as default if the transmission characteristics of the PTR-MS systems are not available. Whether the higher sensitivity at lower E/N values is merely due to the changed kinetics in the drift tube, or if other processes play a role, should be discussed by such an analysis as well.

1: In principle we agree that having a comparison to the theoretical calibration factors would be interesting and useful. We recognize that experimental and theoretical calibration factors do not agreed well under all conditions and it would be informative to know if our study was one of those situations. However, the lack of highly accurate kinetics data makes a representative comparison between the experimental data and theory illusive.

For example, using ion-molecule kinetics to estimate sensitivity, based on the drift tube conditions at 132 Td discussed in this paper, and the kinetics from Mackay et al. (1978) we obtain a calibration factor for acetic acid (at m/z 61) of 23.2 ± 7.0 ncps/ppbv. Using the lower bound of this figure (16.3 ncps/ppbv), and assuming ~50% fragmentation to m/z 43 (reducing the calibration factor at m/z 61 to 8.2 ncps/ppbv), it would be possible to conclude that the results of this study, as well as de Gouw et al. (2003) are comparable to theory, but at the lower bound of the predicted range. At E/N of 88 Td the theory predicts 34.9 ± 10.4 ncps/ppbv, which is similar to the 30.8 ± 2.6 ncps/ppbv found in this work, but again, the uncertainty in the kinetics is so large that a specific conclusion is hard to reach. It would certainly strengthen this work to provide an in depth comparison of the theoretical and measured values, but there is not enough information to provide a high quality, detailed analysis.

Technical Corrections:

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Page 4640, line 10: Lee et al. (2006)...

4642, 6: correct sentence 'The primary...'

4643, 9: report ID rather than OD

Fig 1 caption: Delete sentence 'The regular...'

Fig 4: It is very hard to distinguish between acetic acid and acetonitrile. I suggest to present the same 1-hr acetic acid style as in the other three charts.

The technical suggestions are appreciated and the issues have been rectified in the final manuscript. With regard to figure 4, the color scheme has been changed so that acetonitrile contrasts against the color of the acetic acid data. The high resolution measurements are an important feature, as they show changing in mixing ratio periodically occur on short timescales.

References:

de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, *J. Geophys. Res.*, 108, 4682-4700, doi: 10.1029/2003jd003863, 2003.

Mackay, G. I., Hopkinson, A. C., and Bohme, D. K.: Acid catalysis in the gas phase: dissociative proton transfer to formic and acetic acid, *J. Am. Chem. Soc.*, 100, 7460-7464, doi: 10.1021/ja00492a003, 1978.

Interactive comment on *Atmos. Meas. Tech. Discuss.*, 5, 4635, 2012.

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