

Interactive comment on “Formaldehyde measurements by Proton Transfer Reaction – Mass Spectrometry (PTR-MS): correction for humidity effects” by A. Vlasenko et al.

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We would like to acknowledge Referee#2 for many constructive comments and corrections, which help to improve the manuscript. We are however concerned about the suggestion to do a comparison between equilibrium and time-dependant approaches. The limitation of the equilibrium approach was illustrated by Fig.1 of the original manuscript. The reason that it worked earlier (*Inomata et al. 2008 ACP*) is due to the adjustment of parameter b in a semi-empirical fit of $m/z31$ sensitivity as a function of water vapor concentration. We could follow the same approach and use a reciprocal function $y=5/(x+5)$ to fit our laboratory data on sensitivity (Fig.5). Even though the semi-empirical fit might

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be good, we think that our original analytical approach, which is based on first principles, is more appropriate.

Specific comments: We will retrace our response along the comments made by this referee.

Page 967, line 6. Include the abbreviation TDL here since you use TDL later in the manuscript.

Text added

Page 967, line 19. Consider revising this sentence to: However, because the PA difference is sufficiently small, < 30 kJ, (Spanel and Smith Rapid Commun. Mass Spectrom. 18, 1869, 2004) the back reaction of protonated HCHO with water (R1a) becomes relevant and reduces the sensitivity of detection.

Text is revised and the reference is added .

Page 968, line 17. It should be “hollow” cathode not hallow cathode.

Typo is corrected.

Page 968, line 23. Historically E/N was the abbreviation where N was capitalized. I believe n is usually reserved for the abbreviation of mole.

We agree that E/N is a common abbreviation in literature. Air density is denoted by N .

Page 972, line 21. Replace the approximately equal symbol to \gg . It should read $kR1a[H_2O] \gg kR1[HCHO]$.

Corrected.

Page 972, line 23. The assumption is valid regardless of where the water comes from, the ambient surroundings or leakage from the ion source. The assumption that is being made is that the concentration of water used in the equation can be determined from ambient humidity measurements if the water originates predominately from the

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ambient surroundings.

This is true – the assumption of water origin is not necessary and it is removed.

Page 975, line 8. There is a mistake in the description of the amount of water originating from the ion source. The deduced value of 0.3 hPa refers to an absolute humidity measurement in the ambient sample. The water leaking into the source is equivalent to that amount of water in the ambient sample. If 0.3 hPa actually came from the ion source then it would represent 14% of the total drift tube pressure (0.3/2.13). The mixing ratio computed for 0.3 hPa of water in 1atm of gas is 3×10^{-4} , which would represent 0.03% of the total drift tube pressure.

We agree with referee comment. The estimation of water leakage into drift tube based on pressure difference measurement is not correct. We removed the original statement from the manuscript.

Page 975, 2nd paragraph. The amount of water originating from your ion source may be and probably is much lower than that of others, but it is incorrect to conclude this result by comparing count rates of the $H_3O^+(H_2O)$ m/z 37 ion of your instrument to that of others without verifying that all of the instruments were operated under the same conditions of ion source water flow, drift tube temperature and E/N. Drift tube temperature is a critical variable that is not adequately captured through the E/N term. Comparing your m/z 37 signal that was measured at 323K to those of older instruments that were operated at lower temperatures (room temperature – 313K) is not meaningful and leads in part to the great disparity in the results that you note. I suggest that you eliminate most of this discussion. If you want to actually compare water levels you should go back to those references and try to extract relevant water mixing ratios. What's important to mention is that improvements in the vacuum system made by IONICON has mitigated most of the water leakage from the hollow cathode ion source. Because of these changes, new instruments like yours are significantly less affected than the older PTR-MS instruments.

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We are in agreement and have added text explaining the qualitative nature of the water dimer comparison.

Page 976, eqn 4. I would ask that you restate that you used 1.4×10^{-9} ml/s as the rate constant again. Readers don't often actually read entire papers and might not think to return the discussion of eqn. 1 to find this value.

Text added.

Page 976, line 12. My experience with different PTR-MS instruments is that they are all different and that you should use the transmission factors supplied with your instrument.

The PTR-MS ion transmission curve has a quite steep increase for smaller masses ($19 < m/z < 80$) so it would be desirable to constrain it by measurement in this range. The curve provided by the manufacturer was calculated based on VOCs detected at m/z higher than 79. Ammann et al. (2004) measured transmission factors for smaller masses, such as m/z 33, 45, 59. While the difference between different systems might be taken into account we prefer to use an experimentally constrained value over a mass range closer to that we are considering. We also want to point out that the difference between relative transmission factors is very small, less than 10%.

Page 976, first sentence in Section 3.4. Consider revising this sentence to: The influence of water on the measured and calculated response sensitivities to HCHO is given in Fig. 5.

Text changed.

Page 977, line 9. HCHO should not react with $H_3O^+(H_2O)$ via direct protonation because this reaction is significantly endothermic. The Midey et al. reference is the primary reference and should be cited for which reaction channels are relevant.

Text is changed so that only the possibility of a ligand switching reaction between water dimers and HCHO is mentioned.

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Page 977, paragraph starting on line 17. The humidity dependence described by Warneke et al. for benzene and toluene is not due to the presence water directly, but originates because neither benzene or toluene react with $H_3O^+(H_2O)$. Since the population of $H_3O^+(H_2O)$ ions in your drift tube is so low, one would not expect to see any change in response with changes in humidity.

This is indeed the case. This point will be added to text.

Page 987, Fig. 5 caption. On the last line, toluene is misspelled.

This mistake is corrected.

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