**Atmospheric
Measurement
Techniques
Discussions**

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

Anonymous Referee #2

Received and published: 3 May 2010

The influence of humidity on the measurement of formaldehyde (HCHO) and other compounds possessing similar proton affinities such as HCN and H2S via proton transfer with H3O+(H2O)n is now well known and has been discussed in numerous other publications. Because proton transfer reactions are equilibrium reactions when the proton affinity difference becomes sufficiently small $< \sim$ 30kJ (Spanel and Smith Rapid. Commun. Mass. Spectrom. 18, 1869, 2004), the reverse reaction becomes important and leads to a loss of detection sensitivity. The loss of detection sensitivity is not constant and depends on the amount of water present. There are numerous publications relating to the issues of using a PTR-MS to quantify the concentrations of low proton affinity compounds in the presence of variable humidity levels. The current manuscript

does an acceptable job of acknowledging and discussing most of these. In addition to these papers, it should be noted that Spanel and Smith have a series of papers in Rapid Communications in Mass Spectrometry that pertain to HCHO (Vol 13, 1999), HCN (Vol 18, 2004) and H2S (Vol 14, 2000) where they discuss the quantification of these compounds in humid air using the selected ion flow tube technique. While there are important fundamental differences in flow tube versus drift tube techniques the underlying ion chemistry remains the same and I feel that the flow tube literature should be appropriately referenced.

The current manuscript builds upon of the work of Inomata et al. (Atmos. Chem. Phys. 8, 273-284, 2008). This manuscript notes that Inomata et al. assumed that equilibrium conditions apply and that this assumption is not valid under all relevant measurement conditions and recommends that a time dependent solution should be used. As was noted in the manuscript, the time dependent solution (eqn. 3) is equivalent to that reported by Knighton et al. (Int. J. Mass Spectrom. 283, 112-121, 2009); where they addressed the humidity corrections for the quantification of HCN using a PTR-MS. If one recognizes that the humidity dependence only depends on the proton affinity of the substrate and not its identity (HCN vs HCHO) then it will be apparent that the present manuscript does not offer much in the way of new insight into the measurement of formaldehyde with the PTR-MS. For example, eqn. 3 could have been derived by analogy from the results reported by Knighton et al. As critical as my comments are above, I do recognize that this manuscript is actually well presented and could be beneficial to AMT readership with suitable revision. While model calculations are presented to demonstrate that equilibrium conditions are not achieved under low sample stream humidity, the authors do not explore to what extent the data are improved by correction using the time dependent solution versus the equilibrium approximation. I believe that an inclusion of section where the field data are evaluated using the proposed time dependent and previously reported equilibrium based algorithm (Inomata et al.) would significantly enhance the value of this manuscript. Such a discussion would demonstrate to what extent previous data may be in error as well as illustrating

what improvements might be expected by using the proposed time dependent solution. I would be supportive in recommending publication of a revised manuscript that addressed the aforementioned request as well as the more specific minor comments listed below.

Minor Comments

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

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.

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

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.

Page 972, line 21. Replace the approximately equal symbol to ». It should read $k_{R1a}[H2O] » k_{R1}[HCHO]$.

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 ambient surroundings.

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 $\sim$ 3x10-4, which would represent 0.03% of the total drift tube pressure.

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 H3O+(H2O) 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.

Page 976, eqn 4. I would ask that you restate that you used 1.4x10-9 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.

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.

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.

Page 977, line 9. HCHO should not react with H3O+(H2O) via direct protonation be-

cause this reaction is significantly endothermic. The Midey et al. reference is the primary reference and should be cited for which reaction channels are relevant.

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.

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