**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.

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Received and published: 21 July 2010

We thank the Reviewer#4 for his/her helpful comments and positive evaluation of our manuscript.

Specific comments:

(1)Page 974, Lines 4-7: The amount of water vapor should be expressed by the mixing ratio which unit is mmol/mol, for example. According to this, the x-axis in Figures. 2, 3, and 5 should be replaced with the mixing ratio.

This is a good suggestion. For the sake of consistency it is better to operate with one

type of units, which is in this case mixing ratios. We made changes accordingly to the referee request.

(2)Page 975, Lines 9-13: Since the authors used "hPa" as a unit of the water vapor content , the discussion on the water vapor content from the ion source is confusing. If the mixing ratio is used instead of the pressure, I guess that $[H_2O]_{ionsource}\sim$ 0.3 mmol/mol (= 0.3 hPa/1013 hPa). I think that the number "3 %" may be wrong and that it is probably "0.03 %". With regard to the sentence starting with "This corresponds well to: : :.", the flow system of PTR-MS is not simple because there are two pumping ports at the ion source and the end of the drift tube.

Similar point was brought up by Referee#2. There was a misinterpretation of pressure difference measurement in the original manuscript. For the reasons explained by the Referee (two pumping ports at the ion source) we discarded the results of the pressure difference measurement and removed the statement about agreement. The amount of water, originating from the ion source and estimated using m/z 37 signal, is 0.03% of the total drift tube pressure.

(3)Page 977, Line 28-Page 978, Line 3: Did the authors use the k_{R1a} value of 6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} instead of the literature value (3×10^{-11} cm^3 $molecule^{-1}$ s^{-1}) from Hansel et al. (1997) in the correction? Please clarify this here. And if so, it is better to mention it in Conclusions, too. Another point is that Inomata et al. (2008) obtained the humidity dependence of the detection sensitivity for formaldehyde by PTRMS experimentally, and then fitted the experimental data by a function assuming the equilibrium. In the present method, agreement between the experimental data and the kinetic function is not good (Fig.5), resulting in a systematic error, i.e. the detection sensitivity is overestimated at lower [H_2O] while that is underestimated at higher [H_2O]. In Inomata et al. [2008], even when the data were fitted by a function of the time dependent solution (Inomata et al. (2007)), differences in these two fitting curves (by the functions assuming the equilibrium and the time dependent solution) were at most 5 % in the water vapor concentration range of 5 and 30 mmol/mol.

To clarify the first point we added the value of backward reaction k_{R1a} to the captions of Fig.6 and Fig.2. With regard to the second point we would like to mention that the starting conditions (data comparison before correction) were different for the study of Inomata et al. and the present work. In the work of Inomata et al. (2008) the humidity correction was significantly smaller than in the present study, i.e. after the correction the slope increased 23% from 0.76 to 0.99 (*Inomata et al. 2008 Fig.6*). In our case the correction was much higher, i.e after correction the slope increased almost factor five, from 0.2 to 1.15. Therefore, we consider the positive systematic error of 15% to be satisfactory, bearing in mind possible interferences. To explain the small (5%) difference between time-dependant and equilibrium correction fits we suggest considering the absolute humidity during sampling. If majority of field data points are collected at high humidity (>15 mmol/mol) then the correction will be small (Fig.2).

(4)Page 978, Lines 17-19: With regard to the sentence starting with "With the help of: : :.", the limitation of the assumption of equilibrium depends on the condition of the drift tube, i.e., the reaction time. And if the k_{R1a} value is 6×10^{-11} cm^3 molecule^{-1} s^{-1} , the limitation will also change. Please revise the sentence properly.

This is a good point and we revised the conclusion, specifying that this particular humidity threshold of 15 mmol/mol was calculated for conditions, described in this study.

(5)Figure 2: If the authors concluded that the k_{R1a} value is 6×10^{-11} cm^3 molecule^{-1} s^{-1} better than 3×10^{-11} cm^3 molecule^{-1} s^{-1}, I recommend addition of a line for k_{R1a} value is 6×10^{-11} cm^3 molecule^{-1} s^{-1} in the figure. With regard to the number density of H_3O^+ in the drift tube, it can be estimated to be approximately 5×10^5 molecule cm^{-3} ($=10^7/(10^4\times\pi\times(0.025)^2$) when the signal intensity of H_3O^+, the drift velocity of H_3O^+, and the diameter of the orifice at the end of the drift tube are assumed to be $10^7 cps, 10^4$ cm s^{-1}, and 0.5 mm, respectively. I feel that the value of 1×10^4 ions cm^{-3} reported by Steinbacher et al. (2004) is realistic but that the values of 1×10^{10} and 1×10^8 ions cm^{-3} seem to be unrealistic.

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High values (10^{10}) of H_3O^+ reagent ion concentration were removed. We used the suggested value of 5×10^5 ions cm^{-3} and made a new calculation. The results are very similar which is not surprising since H_3O^+ ions are in excess. Figure 2 was updated.

Technical comments:

(1)Page 967, Line 20: a selected-ion flow tube (SIFT) → a selected-ion flow drift tube (SIFDT)

This is corrected.

(2)Page 972, Line 21: $k_{R1a}[H_2O] \sim k_{R1}[HCHO] \to k_{R1a}[H_2O] >> k_{R1}[HCHO]$

This typo is corrected.