**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.

S. Inomata (Referee)

ino@nies.go.jp

Received and published: 10 May 2010

This paper describes a method to correct the sensitivity of PTR-MS detection of formaldehyde that strongly depends on humidity in air samples. Although an interpretation of the humidity dependence for formaldehyde by the kinetic approach was published by Inomata et al. (2008), they assumed equilibrium between the forward reaction (R1) and the backward reaction (R1a). In this paper, the authors considered kinetics of reaction (R1) and reaction (R1a) and applied the exact kinetic equation (Eqn. (2)) for humidity dependence of the detection sensitivity of formaldehyde. The present method was validated by comparison of results by PTR-MS with those by a

Hantzsch fluorescence monitor in both laboratory and field measurements. The paper is generally well-written. I recommend this paper for publication in Atmospheric Measurement Techniques after the authors' consideration of my specific and technical comments detailed below.

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.

(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 $[H_2O]_{ionsource} \approx 0.3$ 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.

(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 PTR-MS 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$_2$O] while that is underestimated at higher [H$_2$O]. 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.

(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.

(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} = 6×10^{-11} cm^3 molecule^{-1} s^{-1} in the figure. With regard to the number density of H$_3$O$^+$ 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$_3$O$^+$, the drift velocity of H$_3$O$^+$, 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.

Technical comments:

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

(2)Page 972, Line 21: k_{R1a}[H$_2$O] $\approx$ k_{R1}[HCHO] —> k_{R1a}[H$_2$O] $>>$ k_{R1}[HCHO]

References:

Hansel, A., Singer, W., Wisthaler, A. Schwarzmann, M., and Lindinger, W.: Energy dependencies of the proton transfer reactions H$_3$O$^+$ + CH$_2$O $\leftrightarrow$ CH$_2$OH$^+$ + H$_2$O, Int. J. Mass Spectrom. Ion Processes, 167/168, 697–703, 1997.

Inomata, S., Tanimoto, H., Kameyama, S., Tsunogai, U., Irie, H., Kayana, Y., and Wang, Z.: Interactive comment on "Technical Note: Determination of formaldehyde mixing ratios in air with PTR-MS: laboratory experiments and field measurements" by S. Inomata et al., Atmos. Chem. Phys. Discuss. 7, S7047–S7049, 2007,

http://www.atmos-chem-phys.net/7/S7047/2007/

Inomata, S., Tanimoto, H., Kameyama, S., Tsunogai, U., Irie, H., Kayana, Y., and Wang, Z.: Technical Note: Determination of formaldehyde mixing ratios in air with PTR-MS: laboratory experiments and field measurements, Atmos. Chem. Phys. 8, 273–284, 2008,
http://www.atmos-chem-phys.net/8/273/2008/

Steinbacher, M., Dommen, J., Ammann. C., Spirig, C., Neftel, A., and Prevot, A. S. H.: Perfomance characteristics of a proton-transfer-reaction mass spectrometer (PTR-MS) derived from laboratory and field measurements, Int. J. Mass Spectrom. 239, 117–128, 2004.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 965, 2010.