

***Interactive comment on* “Technical Note:
Determination of formaldehyde mixing ratios in
polluted air with PTR-MS: laboratory experiments
and field measurements” by S. Inomata et al.**

Anonymous Referee #2

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The measurement of formaldehyde with a proton transfer reaction mass spectrometer (PTR-MS) is complicated by the low proton affinity of HCHO. The paper describes the detection sensitivity of the instrument as a function of different drift tube voltages and humidities of the sample gas. It also discusses possible fragment masses which could interfere with m/z 31, the protonated mass of formaldehyde. Using this information they compare ambient in-situ PTR-MS measurements with the remote sensing MAX-DOAS technique. Although there is relatively good agreement between the two techniques this intercomparison can not be used to validate the PTR-MS measurements. MAX-DOAS measurements have still larger uncertainties and air masses measured with the two techniques can be different. No attempt has been made here to extract data from

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possibly similar air masses. Nevertheless, the paper contains some valuable information for the PTR-MS community and deserves publication in ACP after the authors have considered the comments below.

Comments:

1. Page 12850, line14: Revise to "into the drift tube";
2. Page 12853, line20: What was the loss of HCHO in this long inlet line?
3. Page 12857, lines 10-16: This discrepancy between direct introduction and dilution is intriguing. Could it be that the mass flow controller of the dilution flow was operated at the lower end, where accuracy is not that good as stated? This could be an alternative to losses in the MFC.
4. Page 12857, lines 17-23: formaldehyde has a dipole moment. Thus the reaction rate constant is most probably higher than $k=2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This implies then that there would also be a difference between calculated and measured sensitivity at $U_{\text{drift}} = 400 \text{ V}$. It is not clear why the backward reaction should become more important with higher E/N because the reaction time in the drift tube decreases. How do the authors interpret that?
5. Page 12857, line29: The authors calculate that 26% of HCHO is measured. However, this is based on the measurement with the dilution method which is assumed to be to low by a factor of 2.7. Using the "correct value" from the direct introduction would yield a much higher value.
6. Page 12558, line 17: The authors assume equilibrium. Does this really apply to all conditions? A justification should be given. There is also the problem with the different b-values as mentioned on page 12860, line 5. Could that be due to a non-equilibrium situation?
7. Page 12863, line 1 and Table 2: The uncertainty values in Table 2 seem not to be in percent to comply with the values in line 1 of page 12863.

8. Page 12876, Figure 6: add labels to the figure axes.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 12845, 2007.

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