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Atmospheric Chemistry and Physics Discussions

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 #1

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General comments

The paper by Inomata et al. presents a detailed calibration of a proton transfer reaction mass spectrometer (PTR-MS) for measurements of atmospheric formaldehyde mixing ratios. It also presents new results from an intercomparison field experiment where formaldehyde mixing ratios were measured using the in situ PTR-MS technique and a remote sensing technique called multi-axis differential optical absorption spectroscopy (MAX-DOAS).

The PTR-MS is capable of measuring numerous volatile organic compounds in air with a high sensitivity and a fast time response. It is a novel instrument that has already

proven to be a valuable tool in atmospheric research. Formaldehyde is an important component of tropospheric chemistry. It is a difficult compound to detect by PTR-MS since its detection sensitivity is low and humidity dependent due to the non-negligible backward proton transfer reaction in the PTR-MS drift tube. So far, a direct calibration of the PTR-MS for formaldehyde has not been published.

Since the authors have determined the humidity dependent detection sensitivity for formaldehyde in different operating conditions of the PTR-MS and have discussed the possible interference caused by other compounds in the sampled air, their paper gives significant new information to the growing PTR-MS user community. The results of the intercomparison experiment were new and interesting but they can hardly be used as a validation of the PTR-MS measurements. This stems from the fact that the in situ PTR-MS measurements were compared with the remote sensing MAX-DOAS measurements. In addition, it seems that also MAX-DOAS has several sources of uncertainty, and the consequent errors are difficult to estimate very accurately. I was happy to notice that these drawbacks were acknowledged in the manuscript.

Generally, the manuscript is clearly laid out and well written. However, some parts of it have to be clarified or revised. Overall, I believe that the paper by Inomata et al. merits publication in Atmospheric Chemistry and Physics after the authors have considered the specific and technical comments below.

Specific comments

1. Page 12845, the title of the manuscript. Is it necessary to refer to polluted air in the title? The paper does not discuss actual pollution or air quality measurements, and I suppose that the given information applies to all atmospheric measurements by PTR-MS.

2. Page 12847, lines 11-24. The authors could also mention that formaldehyde is probably carcinogenic (e.g. Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons, Inc., New York,

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1998), which increases the motivation for formaldehyde measurements especially in urban areas. In this respect, the current title of the paper might be appropriate.

3. Page 12852, lines 20-22. It does not become clear from the text why the high purity N_2 gas was needed in the laboratory calibration.

4. Page 12853, lines 4-10. Since only methanol, ethanol, and methyl hydroperoxide are mentioned before, the role of the other compounds should be clarified.

5. Page 12853, lines 20-21. Add the length and the inner diameter of the sample line, as well as the sample flow rate.

6. Page 12856, lines 19-21. The sentence starting with "In all..." is vague and should be revised. Could the authors briefly explain the negative values in Figure 2?

7. Page 12857, lines 10-13. I believe that the concentration of 1.02 ppmv used in the direct introduction method is close to the upper limit of the linear dynamic range of the PTR-MS. If this was supposed to cause the possible saturation of the ion signal, it should be stated more clearly in the text.

8. Page 12859, lines 22-25. Could the authors explain more explicitly why the term m/n is used in Equation (7)? Also the origin of the term $1/23.3$ could be stated more clearly.

9. Page 12860, line 3. The errors originating from the fitting to Equation (4) are not presented in Figure 4.

10. Page 12860, line 23. Table 2 is unnecessary since all the information is given in the text.

11. Page 12863, lines 1-2. Where do the values 0.07, 0.03, and 0.09 come from? I believe that $\delta\alpha_{49}\alpha_{49}$ should be $\delta\alpha_{49}/\alpha_{49}$ and so on.

12. Page 12863, lines 5-6. Since the values of the slope and the intercept are given in the abstract, both of these values should be given also here.

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Technical comments

1. Page 12846, line 8. Would "calibration of PTR-MS for HCHO" be better than "calibration of HCHO by PTR-MS"?

2. Page 12847, line 10. Should the reference "Lee et al., 2006" point to "Lee et al.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, Journal of Geophysical Research, 111, D17305, doi:10.1029/2006JD007050, 2006." instead of the paper in the reference list?

3. Page 12848, lines 4-5 and 24-25. Add commas or dots to the references.

4. Page 12849, line 20. Revise to "...calibration of PTR-MS...".

5. Page 12858, lines 18, 21, and 25. Use the same notation for protonated formaldehyde as in Reactions (R6) and (R-6).

6. Page 12859, line 9. The phrase gives a wrong impression that the fitting parameter a was calculated using the reaction rate constants and the formaldehyde concentration.

7. Page 12861, lines 7, 12, and 13. Revise I_X to I_{31} and X to 31.

8. Page 12866, lines 26-29. Correct the pages of the reference "Irie et al. (2007)" to 9769–9793.

9. Page 12872, caption. Add "in dry conditions" after "...E/N ratios...".

10. Page 12874, figure and caption. The formaldehyde concentration could be mentioned. The errors are not presented in the figure.

11. Page 12876, figure and caption. Add the labels of the y- and x-axes, as well as the legends a and b. The error limits are not presented in the figure.

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