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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sample drying to improve HCHO measurements by PTR-MS instruments: laboratory and field measurements" *by* B. T. Jobson and J. K. McCoskey

Anonymous Referee #2

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This paper describes an application of an inlet system for drying air sample. A cold trap is used to condense and freeze water vapor in ambient sample air before being directed to a PTR-MS instrument in on-line measurements of VOCs, especially HCHO. The authors showed the enhancement of the detection sensitivity of HCHO by this technique, leading to the improvement of the HCHO measurements by PTR-MS. They also found that losses of VOCs at the water trap were not significantly observed for many kinds of VOCs except specific compounds, by setting the temperature of the water trap to -30 $^{\circ}$C and by taking an enough conditioning period in which the tube of the water trap becomes passivated. In particular, a very interesting property of the water trap is shown for HCHO in Figure 3. The technique presented here provides significant merits in the

PTR-MS measurements of VOCs in ambient air: (1) we don't need to be bothered by the humidity dependence of the detection sensitivity for VOCs, (2) the detection sensitivity for species which proton affinity is close to that of water vapor (e.g. HCN, CH_3I besides HCHO) will be improved compared to that in humid sample, and (3) a field strength of a drift tube in PTR-MS can be operated at low *E/N* ratios, resulting in an increase of the detection sensitivity for VOCs as well as less fragmentations for fragile species. Although I think that some parts of the paper have to be clarified or revised, the paper is useful for the PTR-MS community of atmospheric chemistry. I recommend this paper to be published in Atmospheric Chemistry and Physics after the authors' consideration of my specific and technical comments detailed below. If I understand the journal's publication policy correctly, I think that "Technical notes" are more appropriate because the paper describes "novel aspects of the experimental technique" rather than "substantial new results and conclusions from scientific investigations of atmospheric properties and processes".

Specific comments:

(1) Page 19849, Line 19 and Page 19851, Lines 9−13: Didn't the authors use ion transmission efficiencies through the quadrupole which were probably provided by the manufacturer, Ionicon Analytik? If not, the calibrated sensitivity should not be compared with the calculated sensitivity.

(2) Page 19850, Line 6: What kinds of VOCs are included in the 13 component VOC standard? In Tables 1 and 2, there are 14 VOCs except formaldehyde. This seems to be inconsistent.

(3) Page 19850, Lines 24−26: Midey et al. (2000) reported that the ligand switching is the only product ion of the $H_3O^+(H_2O)$ reactions with acetaldehyde. However, I cannot find that Midey et al. (2000) mentioned the subsequent dissociation to produce protonated acetaldehyde.

(4) Page 19851, Lines 15−16: The authors mentioned that the observed benzene sensitivity agreed with the calculated one after the authors used a new ion detector although there was difference between the observed and calculated benzene sen-

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sitivities using an old ion detector. Did this change of the sensitivites occur only for benzene? How about other VOCs? I found the difference in the detection sensitivities of HCHO in Table 2 and in Figure 3 (11.3 v.s. $\sim$13 Hz/ppbv per MHz H_3O^+). Is this difference also caused by the change of the ion detector?
(5) Page 19855, Lines 26$-$29: What are "conditioning effects"? Is one of them that 100 % transmission of VOCs through the water trap becomes possible? What are others? In addition, I cannot follow the sentence starting from "For example, ...". Did the author here want to mention that the absorption of HCHO to the Silonite coated steel tubing occur at the first stage of the conditioning period, then the tube becomes passivated, which allows 100 % transmission of HCHO? Please clarify.
(6) Page 19857, Line 24 – Page 19858, Line 16: I feel that the section of "3.3 Field test" should be moved to Experimental.
(7) Page 19861, Line 7 – Page 19862, Line 6: In the first paragraph of the section "3.6 HCHO interferences", the authors discussed the interference of CH_3OH on *m/z* 31. However, in the second paragraph, I think that the authors did not discuss the influence of CH_3OOH on *m/z* 31. Did the authors conclude that there is no interference of CH_3OOH on *m/z* 31 at 100 Td and 80 Td? If so, how did the authors check it?
(8) Page 19868, Table 2: Values of normalized sensitivities for "Dehumidified at -30 °C" at 120 Td listed in Table 2 except for HCHO are slightly strange to me. The normalized sensitivity for "Ambient RH" for most VOCs except HCHO had a linear dependence on RH as shown in Fig. 5. The values for "Ambient RH" listed in Table 2 were averaged values in Fig. 5, so the values for "Ambient RH" should be relatively larger than those for "Dehumidified at -30 °C" which correspond to extrapolated values at 0.03×10^5 $H^+(H_2O)_2$ per MHZ H_3O^+ (this value was calculated by using $H^+(H_2O)_2$ = 0.2×10^5 Hz from Fig. 4A and H_3O^+ = 7×10^6 Hz from Fig. 1A) in the figure. When I look at the data in Fig 5, the averaged value for "Ambient RH" and the expected value for "Dehumidified at -30 °C" for acetonitrile, for example, may be $\sim$18 and $\sim$15 Hz/ppbv per MHz H_3O^+, respectively. The value for "Ambient RH" in Table 2 is consistent while the value for "Dehumidified at -30 °C" in Table 2 is slightly large.

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Similarly, the values for "Dehumidified at −30 °C" are slightly large for acetaldehyde and isoprene. Please explain this.
(9) Page 19868, Table 2: Did the authors check a linearity of ion signals against VOC mixing ratios at "Dehumidified at −30 °C" mode?
(10) Page 19871, Figure caption of Fig. 3: I did not find any explanation of "2 different experiments".
(11) Page 19876: Data shown in Figure 8 are shown again in Figure 9. I think that Fig. 8 is not necessary.

Technical comments:
(1) Page 19849, Line 5: Warneke et al. (2001) is missing in References.
(2) Page 19849, Line 21: Su, 1989 → Su, 1988
(3) Page 19850, Lines 16 and 17, Page 19851, Line 1, and Page 19852, Line 5: The "%" was used as a unit of H_2O mixing ratios in these parts, however, "mmol/mol" was used in Table 1 and Figure 1. The authors should unify them.
(4) Page 19851, Line 27, Table 1, and Figure 1 (A): (Td =) 100 → (Td =) 108. Is this correction right?
(5) Page 19854, Lines 4 and 16 and Page 19858, Line 12: Both ml min^{-1} and ml/min are used. The author should unify them.
(6) Page 19857, Line 7: "Staudinger and Roberts, 1996" is missing in References.
(7) Page 19859, Line 26: Hanson et al., 2008 → Hanson et al., 2009
(8) Page 19860, Line 14: Inomata → Inomata et al. (2008)
(9) Page 19861, Line 8: Inomata et al. (2004) → Inomata et al. (2008)
(10) Page 19864, Line 13: . . .Environ. Sci. Technol., "39", 4767. . .
(11) Page 19864, Line 14: Li, J. S. → Li, J.
(12) Page 19864, Line 14: . . .Robust hybrid "flow" analyzer. . .
(13) Page 19864, Line 23–25: Hansel et al. (1995) is not cited in text.
(14) Page 19865, Line 21–23: Kawai et al. (2003) is not cited in text.
(15) Page 19865, Line 27: 1997 → 1998

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(16) Page 19865, Line 29: . . ..J. Phys. Chem. “A”. . ..
(17) Page 19866, Line 1: reactions → Reactions
(18) Page 19866, Line 13: 1989 → 1988
(19) Page 19866, Line 14: All authors’ names should be put.
(20) Page 19866, Line 14: “A study of” formaldehyde. . ..
(21) Page 19866, Line 18: MS “–” measurement,. . ..
(22) Page 19866, Line 21: All authors’ names should be put.
(23) Page 19866, Line 22: 8 → 4104

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 19845, 2009.