

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

B. T. Jobson and J. K. McCoskey

tjobson@wsu.edu

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Response to Anonymous Referee #2.

Thank you for your thorough reading of this paper.

(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.

We did not measure the transmission curve. Our ETP multiplier aged rapidly at high

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ion count rates causing problems with ion transmission tests where the reagent ion is titrated away. We don't have a quantitative explanation for the differences between observed sensitivity and measured. To avoid being speculative we removed the sentence “The lower observed sensitivities were likely due to differences in H₃O⁺ and C₆H₇⁺ ion transmission efficiencies through the quadrupole and differences in detector sensitivities to these ions.”

(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.

This should have read 14 component VOC standard. The components are those listed in Table 1. Text on page 19850 was corrected to read “. . . 14 component VOC standard. . .”

(3) Page 19850, Lines 24–26: Midey et al. (2000) reported that the ligand switching is the only product ion of the H₃O⁺(H₂O) reactions with acetaldehyde. However, I cannot find that Midey et al. (2000) mentioned the subsequent dissociation to produce protonated acetaldehyde.

This was a poorly worded sentence. What we mean is that Midey has noted fast ligand switching reactions with acetaldehyde (our reaction R5). In the PTR-MS this complex likely dissociates leaving behind protonated acetaldehyde (R6). We changed this sentence to read: “Since the proton affinity of acetaldehyde is lower than that of the water dimer, the likely mechanism is ligand switching (Midey et al. 2000) and 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 sensitivities using an old ion detector. Did this change of the sensitivities occur only for benzene? How about other VOCs? I found the difference in the detection sensitivities

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of HCHO in Table 2 and in Figure 3 (11.3 v.s. \sim 13 Hz/ppbv per MHz H₃O⁺). Is this difference also caused by the change of the ion detector?

Since we don't know our ion transmission curve it is perhaps better not to make these comparisons between measured and calculated sensitivity for benzene and other VOCs. With the new SEM and lower SEM operating voltage, there may be significant differences in the ion transmission curve. We don't know what this curve looks like for the ETP multiplier. These observations are likely only relevant to our instrument with this type of detector and don't offer much information about the PTR-MS instrument in general. To avoid confusion and speculations we removed 2 sentence on page 19851: "The lower observed sensitivities were likely due to differences in H₃O⁺ and C₆H₇⁺ ion transmission efficiencies through the quadrupole and differences in detector sensitivities to these ions." ; "A new multiplier installed for the field experiment resulted in better agreement between observed and calculated benzene sensitivity."

(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.

There is some confusion with use of the plural "effects". We changed this to "effect". Conditioning effects are usually attributed to be losses of analytes to active sites on surfaces, usually due to physical adsorption. A conditioning effect implies that analyte recovery depends on the mass of analyte that has passed through the analytical system. With respect to the water trap the conditioning effects are discussed on page 19856: "Conditioning is a complex surface adsorption process dependent on the nature of the sample including the VOC composition and abundance and the amount of water vapor. For the water trap, the tubes become coated with ice so the interaction of the VOC with ice becomes an important process. "

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This is an awkward sentence. This now reads: "For example, tests with our HCHO + multicomponent VOC test mixture in dry air showed that \sim 10 ng of HCHO adsorbed to the Silonite coated steel tube at -65 °C before the tube was passivated and allowed 100% transmission of HCHO."

(6) Page 19857, Line 24 – Page 19858, Line 16: I feel that the section of "3.3 Field test" should be moved to Experimental.

Section 3.3 was moved into experimental section and re-named 2.3.

(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 CH₃OH on m/z 31. However, in the second paragraph, I think that the authors did not discuss the influence of CH₃OOH on m/z 31. Did the authors conclude that there is no interference of CH₃OOH on m/z 31 at 100 Td and 80 Td? If so, how did the authors check it?

Good point. We were not able to determine the CH₃OOH dissociation artefact on m/z=31 since we did not have a CH₃OOH standard at the time. We now note this explicitly in the second paragraph by adding the following sentences: "The level of interference from CH₃OOH on the m/z=31 ion signal could not be quantified in the field study. This is issue will be the subject of a future study."

(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₊(H₂O)₂ per MHz H₃O⁺ (this value was calculated by using H₊(H₂O)₂ = 0.2×10^5 Hz from Fig. 4A and H₃O⁺ = 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

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per MHz H₃O⁺, 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. Similarly, the values for “Dehumidified at -30 _C” are slightly large for acetaldehyde and isoprene. Please explain this.

To summarize your comment, the trend lines in Figure 5 for the humidity dependence do not extrapolate back to the ncps values listed in Table 2 for the dehumidified calibrations. For the dehumidified calibrations the average normalized water cluster count rates were 4700 ± 800 . The dehumidified calibration values were consistently and significantly greater than the trend line extrapolation.

The reason for the higher than expected sensitivities is that the m21 counts rates were slightly less in dehumidified mode. The average difference was $6.7 \pm 2.3\%$. This is shown in a new figure (Figure 6) depicting 2 field calibration periods: April 20 representing relatively dry conditions and April 25 representing relative humid conditions. We have added the following text to discuss this point:

“For the dehumidified calibrations the average normalized water cluster count rates were 4700 ± 800 . It is noted from Table 2 that the dehumidified calibration values were consistently and significantly greater than the trend line extrapolation to low humidity in Figure 5. The reason for the higher than expected sensitivities is that H₃O⁺ count rates were consistently lower in dehumidified mode. On average H₃O⁺ count rates were $6.7 \pm 2.3\%$ less when sampling through the water trap during calibration periods but there was little difference in the calibration gas ion signal levels, especially for dry conditions. This is shown in Figure 6 where 2 field calibration periods are depicted: April 20 representing relatively dry conditions and April 25 representing relative humid conditions as indicated by the H₊(H₂O)₂ count rates. For benzene (m/z = 79) there was no discernable change in ion signal when the PTR-MS sampled through the water trap for either calibration period. However, the decrease in H₃O⁺ count rates when sampling through the water trap, -7.6% for the April 20 calibration and -4.3% for the April 25 calibration, causes the normalized sensitivity to be greater for dehumidified conditions.

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For acetonitrile (m/z = 42) there was no significant difference in ion signal between ambient humidity and water trap calibration for the April 20 period, thus the dehumidified normalized sensitivity is 7.6% larger because of the difference in H₃O⁺ count rates. For April 25 the ambient humidity calibration displayed a significantly higher count rate than on April 20 and a significant drop in the count rate through the water trap. During this period the H₊(H₂O)₂ ion count rate was 15% of the H₃O⁺ count rate compared to 3.4% for the April 20 ambient humidity calibration. The difference in acetonitrile behavior between the 2 calibration periods is qualitatively consistent with H₊(H₂O)₂ acting a reagent ion. It was clear from the calibrations that the PTR-MS sensitivity in dehumidified mode could not be extrapolated from the ambient humidity trend lines given in Figure 5. “

Full figure caption reads: Figure 6. Acetonitrile (m42, dark squares), benzene (m79, dark circles), H₃O⁺ (open circles) and H₊(H₂O)₂ (open squares) ion signals during calibration. Shown are two different days representing relatively dry (April 20) and humid (April 25) sampling conditions. For both time periods the data show a sequence of ambient air sampling (ambient), followed by zero air sampling (zero), addition of calibration gases (cal), and a final zero air period. The decrease in H₊(H₂O)₂ signal during calibration was due to the addition of dry calibration gas to the humid zero air flow. Sampling through the water trap is apparent by the decrease in H₊(H₂O)₂ count rates. A significant decrease in H₃O⁺ was always observed when sampling through the water trap.

(9) Page 19868, Table 2: Did the authors check a linearity of ion signals against VOC mixing ratios at “Dehumidified at -30 _C” mode?

Yes we did check this. There is a much smaller variation in the water cluster ion count of course and no discernable trend between ncps and normalized water cluster count rates.

(10) Page 19871, Figure caption of Fig. 3: I did not find any explanation of “2 different

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experiments”.

The tests were run on two different days. It is not necessary to note this so we simplified Figure 3 so that the symbols were all of one type and removed “results from 2 different experiments are shown” from the figure caption.

(11) Page 19876: Data shown in Figure 8 are shown again in Figure 9. I think that Fig. 8 is not necessary.

The time series data in Figure 8 are a subsection of Figure 9 to better illustrate the signal to noise. We feel it was an important visualization of the raw data and provides information about the ability of the instrument to resolve small changes in mixing ratio that are hard to see in the 4 week period depicted of 5 minute average data in Figure 9.

Technical comments: (1) Page 19849, Line 5: Warneke et al. (2001) is missing in References. Added.

(2) Page 19849, Line 21: Su, 1989 ! Su, 1988 Corrected.

(3) Page 19850, Lines 16 and 17, Page 19851, Line 1, and Page 19852, Line 5: The “%” was used as a unit of H₂O mixing ratios in these parts, however, “mmol/mol” was used in Table 1 and Figure 1. The authors should unify them. Unified with mmol mol⁻¹

(4) Page 19851, Line 27, Table 1, and Figure 1 (A): (Td =) 100 ! (Td =) 108. Is this correction right? Td=108. Corrected.

(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. Used ml min⁻¹

(6) Page 19857, Line 7: “Staudinger and Roberts, 1996” is missing in References. Added.

(7) Page 19859, Line 26: Hanson et al., 2008 ! Hanson et al., 2009 Corrected.

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(8) Page 19860, Line 14: Inomata ! Inomata et al. (2008) Corrected.

(9) Page 19861, Line 8: Inomata et al. (2004) ! Inomata et al. (2008) Corrected.

(10) Page 19864, Line 13: . . . Environ. Sci. Technol., “39”, 4767. . . Corrected.

(11) Page 19864, Line 14: Li, J. S. ! Li, J. Corrected.

(12) Page 19864, Line 14: . . . Robust hybrid “flow” analyzer. . . Corrected.

(13) Page 19864, Line 23–25: Hansel et al. (1995) is not cited in text. Added to text, page 19846.

(14) Page 19865, Line 21–23: Kawai et al. (2003) is not cited in text. Removed citation.

(15) Page 19865, Line 27: 1997 ! 1998 Corrected.

(16) Page 19865, Line 29: . . . J. Phys. Chem. “A”. . . Corrected.

(17) Page 19866, Line 1: reactions ! Reactions Corrected.

(18) Page 19866, Line 13: 1989 ! 1988 Corrected.

(19) Page 19866, Line 14: All authors’ names should be put. It was editor’s request for this format.

(20) Page 19866, Line 14: “A study of” formaldehyde. . . Corrected.

(21) Page 19866, Line 18: MS “–” measurement,. . . Corrected.

(22) Page 19866, Line 21: All authors’ names should be put. It was editor’s request for this format.

(23) Page 19866, Line 22: 8 ! 4104 Corrected.

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

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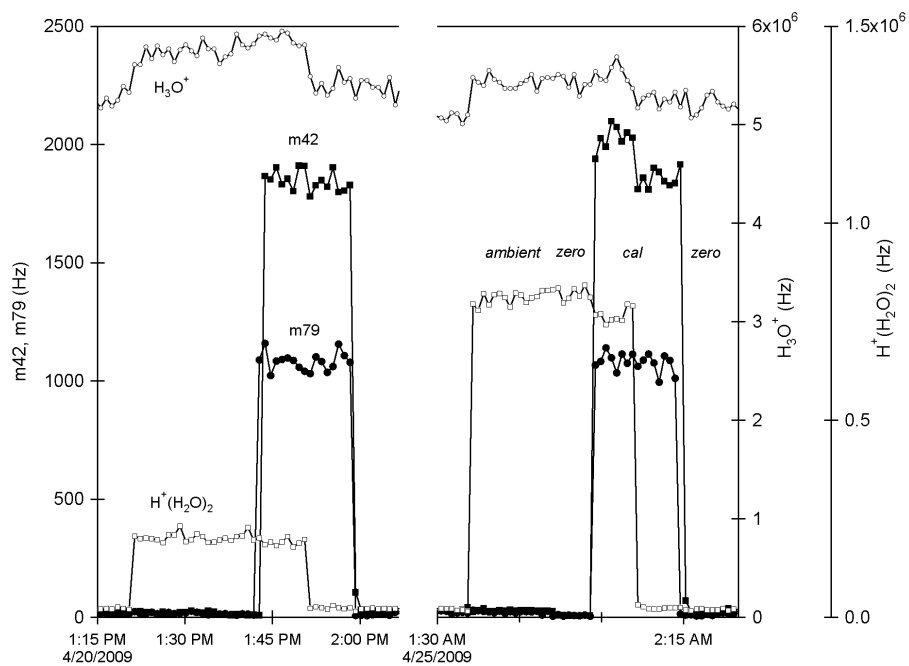


Fig. 1. Figure 6. Acetonitrile (m42, dark squares), benzene (m79, dark circles), H₃O⁺ (open circles) and H⁺(H₂O)₂ (open squares) ion signals during calibration.