

Interactive comment on “Calibration and intercomparison of acetic acid measurements using proton transfer reaction mass spectrometry (PTR-MS)” by K. B. Haase et al.

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Received and published: 12 October 2012

Thank you very much for taking the time to critique our manuscript and provide valuable feedback. Our responses are placed inline with your comments.

Introduction: The authors briefly discuss sources and sinks of acetic acid, but a comment on the typical atmospheric lifetime might be helpful.

1: The lifetime of the acetic acid is dependent on the conditions governing its deposition velocity. Over water and during rain events, the loss rate can be very high, and the lifetime on the order of hours. In dry conditions, the lifetime can be several days. The
C2514

introduction has been modified to reflect this range.

P 4642, line 6-7: can the authors comment on the large differences between the primary ion signals

2: The difference in the ion signals is likely due to the modified flow system, which reduced the amount of skimmer region and ion source ahead of the drift tube, reducing the strength of the H_3O^+ signal. The manuscript has been modified to draw this connection for the reader.

P 4643, line 1: please clarify whether the purified air was ambient or from a cylinder (I assume the former)

3: The manuscript was modified to reflect that ambient air was purified using the catalytic converter.

P 4644, Appledore Island measurements: It isn't clear which mass (or masses) have been used to generate the Appledore Island acetic acid data. Is it just from the m/z 61 signal, from (m/z 61 + m/z 43), or has a correction for fragmentation (m/z 43) been applied? Also, how often were calibrations performed during the campaign period?

4: The signal at m/z 61 was used as for the detection of acetic acid during the period of measurements made on Appledore Island. While the instrument was periodically calibrated using standard mixtures of other compounds during the study, it was not possible to calibrate specifically for acetic acid in that time frame.

P 4644, line 18: I assume the reference to (Haywood et al., 2002) is for the statistical method, i.e. the uncertainty of 9.2 % was derived from your data using the method of Heywood et al.? Please clarify.

5: The manuscript has been modified to indicate that the estimated uncertainty was derived using counting statistics of the background and average signal using the method described in (Hayward 2002).

P 4645, paragraph 1: The detection limits for the high sensitivity version of PTR-1 (0.32 ppb) seem to be higher than those of the standard sensitivity version (0.16 ppb). This seems odd – surely the more sensitive instrument would be expected to have the lower detection limit. Please explain.

6: The difference in detection limits are due to the differences in primary ion signal discussed above. With a lower primary ion abundance in PTR-MS-1, fewer proton transfer reactions take place, yielding few product ions. If the primary ion signal were the same as PTR-MS-2, the limits of detection would be similar. This point has been clarified in the manuscript.

P 4645, line 22: The authors state the reduced diameter of the valve, but what was the difference in the diameter of the tubing? The response times for PTR-1 were pretty poor – is the 6.35 mm valve common in PTRMS instruments? I am slightly surprised that a switch to a slightly smaller valve can have such a dramatic effect. Is this seen for all VOCs, or just for acetic acid?

7: A 1/4" (Teqcom M422C1DTS-LT) valve was used as a replacement for the standard sensitivity instrument after the failure of the OEM 1/8" valve. This valve required a short section of 1/4" teflon tubing to adapt to the 1/8" inlet of the PTR-MS. This valve was eventually replaced with an appropriate diameter valve. From experience with external calibrations, the signal for most compounds stabilized within ~7 minute measurement cycle time.

P 4646, section 3.2: The discussion of fragmentation with respect to E/N is interesting, but I wonder if the authors could explain a little more (for the benefit of non-PTRMS experts in particular) as to the balance between optimising sensitivity and minimising cluster formation and fragmentation for acetic acid measurements. Are they able to recommend some standard or optimal operating conditions?

8: By decreasing the drift tube voltage, the reaction time for H₃O⁺ to interact with an-

C2516

alytes is increased, and there is decreased fragmentation, yielding greater response. However, this effect can be negated by the formation of hydrated clusters that do not readily engage in proton transfer reactions with several analytes and can engage in ligand switching reactions, all of which can complicate the obtained spectrum and quantification target compounds. The response to acetic acid is more favorable at lower field strengths, however, this comes at the loss of easy quantification of many other compounds (like benzene, which is not protonated by higher order clusters), so we do not recommend any particular drift tube setting, only inform the reader of the instruments potential. Additionally, Ionicon has made several revisions of the ion source and drift tube design that transfer different amounts of water vapor to the drift tube, resulting in decreased cluster formation in newer instruments. The result of those changes make it possible that some users may find lower drift tube field strengths more useful than others. As requested, this paragraph has been improved to elaborate on the relationship between drift tube voltage, sensitivity, and cluster formation.

P 4648, Section 3.4: paragraph 1 and 2: Are the authors saying that the performance problems associated with the PTRMS would affect the slope of Figure 3? – or do they just add to the general scatter? Does the fact that the PTR is often higher than the MC/IC (see also Figure 2) suggest there could be a small interferent in the PTR signal – it is not easy to see the uncertainties in Figure 2.

9: The performance problems, particularly the power failures, would likely cause periods of artificially high measurements which could explain the positive slope of the (PTR-MS/MC-IC) ratio. The high background signal at m/z 61 after power outages and the overall high signal during the campaign are remarkable, especially when compared to data obtained with the same instrument in 2010 (see below for 2004 and 2010 data comparison). These performance issues experienced are significant enough that they could be masking the degree of interference from other compounds. It is possible that there is a non-acetic acid enhancement at m/z 61, however, that interference would likely need to have a similar, closely linked relationship with acetic acid over time, since

C2517

the PTR-MS data does not show any increases that are not also reflected in the MC/IC results. The paragraph in the manuscript has been modified to include consideration of the possibility of interference from other compounds. (see Figures for 2010 (fig 1) and 2004(fig 2), below)

P 4648, line 23-26: please state whether this paragraph refers to the PTRMS measurements only. 10: From this point on in the manuscript, only PTR-MS measurements of acetic acid are discussed. This point has been clarified in the discussion of the statistics for the campaign.

P 4649, ICARTT 2004: the discussion of the ICARTT data is rather short, although this is probably acceptable for an instrument paper of this type. However, are the acetic acid measurements discussed in more detail elsewhere? If so, please give a specific reference.

11: We do agree that the discussion of the ICARTT acetic acid data is abbreviated, however, analyzing that data in detail is beyond the scope of this manuscript and would be the topic of a future publication. There is some additional discussion of these measurements of acetic acid with respect to meteorology that appear in (Haase 2010), and several of the other compounds measured, but not acetic acid, appear in (Chen et al. 2007) as referenced in the submitted draft. A reference to this has been added to the manuscript for completeness.

In the text the mixing ratio units are normally given as ppbv, whilst in Figures 2, 3 and 4 they are in pptv.

12: The movement between ppbv and pptv was unintentional. The graphs have been reconstructed in units of ppbv.

Technical Corrections:

P 4638, line 3: delete the word “precursors” and make “alkene” plural.

P 4637, line 24: no comma needed after cloud water

C2518

P 4639, line 25-26: need to put references in date order (check elsewhere as well)

P 4640, line 10: Sentence should start “Lee et al. (2006b) . . .”

P 4643, line 16-17: Do the authors mean “Known mixing ratios of acetic acid were generated by . . .”

P 4645, line 10: should read “. . . and 0.32 ppbv for”.

P 4645, line 23: “mixing ration” should read “mixing ratio”

P 4647, line 18: date missing from Feilberg et al. reference

P 4647, line 27: need full stop after (H2O) and move the subsequent bracket, i.e. “. . . . (H2O). Hartungen et al., (2004)”

P 4648, line 17: add “to”, i.e. “These outages contributed to the variability”

Figure 1: What are the units of elapsed time (x axis)?

Table 1: The temperature of the Maleknia et al study is listed as 630 degrees – is this correct?

Thank you for pointing out the numerous typographical errors and mistakes. We have applied the technical corrections as recommended. Maleknia et al. reported a range of measurements from 30-60 C.

References: Chen, M., Talbot, R., Mao, H., Sive, B., Chen, J., and Griffin, R. J.: Air mass classification in coastal New England and its relationship to meteorological conditions, *J. Geophys. Res.*, 112, D10S05, doi: 10.1029/2006jd007687, 2007.

Haase, K. B.: Calibration, Optimization, and Deployment of PTR-MS Instruments During the AIRMAP Project, Doctor of Philosophy, Chemistry, University of New Hampshire, Durham, 186 pp., 2010

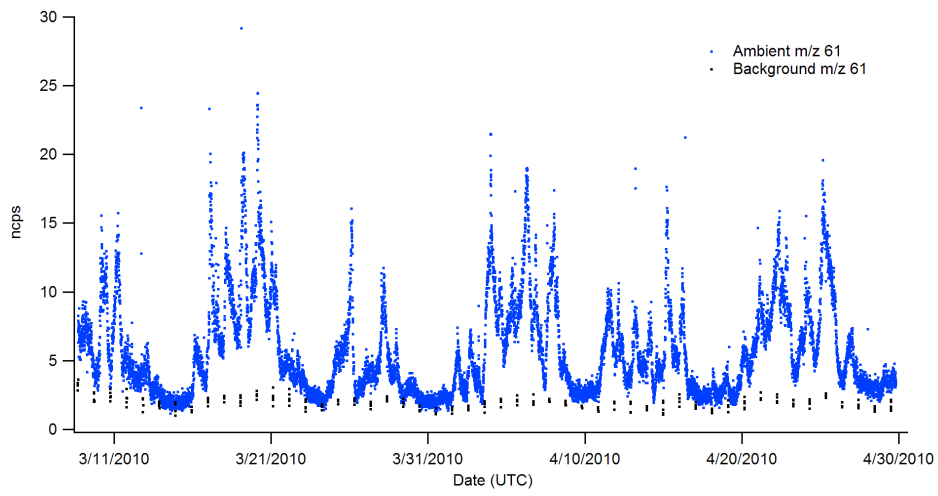


Fig. 1. Typical PTR-MS signal and background at m/z 61 during 2010

C2520

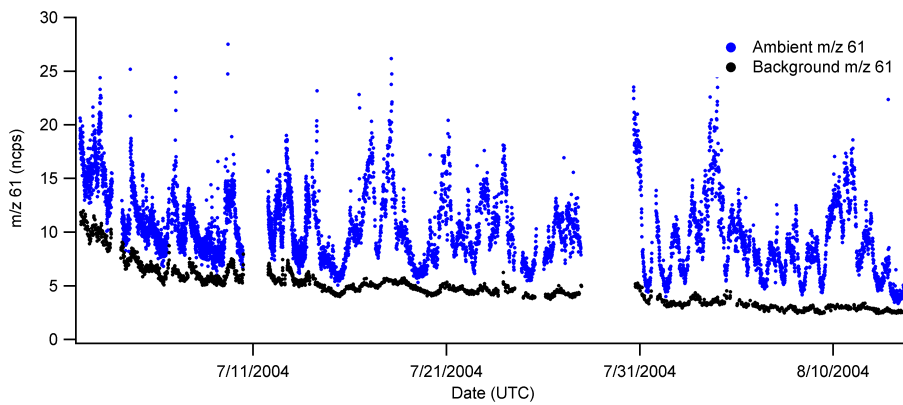


Fig. 2. ICARTT PTR-MS signal and background at m/z 61 during 2004

C2521