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Atmospheric Measurement Techniques Discussions

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

Anonymous Referee #3

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The manuscript explores the potential of the PTR-quadrupole-MS technique for making quantifiable measurements of acetic acid in the atmosphere. Reported measurements of this important organic acid are relatively sparse, owing to the difficulty of sampling and calibration. The PTRMS signal at m/z 61 has long been attributed to acetic acid (together with several potential interferents), but this is one of the first detailed studies to include detailed calibration experiments and a comparison with acetic acid measurements using a second analytical technique (mist chamber/ion chromatography) during a field campaign. The manuscript is generally well written and is a useful contribution to the ever growing literature on the capability of the PTRMS method. I recommend

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publication in AMT following consideration of the comments that follow:

1. Specific comments

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

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

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

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?

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.

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.

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?

P 4646, section 3.2: The discussion of fragmentation with respect to E/N is interesting,

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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?

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.

P 4648, line 23-26: please state whether this paragraph refers to the PTRMS measurements only.

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.

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

2. Technical corrections

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

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

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 . . ...”?

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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?

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 4635, 2012.

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