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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Performance of Chemical Ionization Reaction Time-of-Flight Mass Spectrometry (CIR-TOF-MS) for the measurement of atmospherically significant oxygenated volatile organic compounds" *by* K. P. Wyche et al.

K. P. Wyche et al.

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The authors are grateful to both the referees for the thoughtful and insightful reviews.

All technical corrections have been made in accordance with both of the referee's suggestions.

(1) In line with the referee's wishes *Section 2.1: Experimental* has been extensively rewritten to include an instrument schematic (now Figure 1) and a much more in-depth discussion of the instrument and in particular its custom drift cell (additionally attention is paid to similarities to the design of Hanson rather than the standard Ionicon model).

Additionally all of the further minor issues raised by referee #2 under comments (1) have been addressed as follows:

- The accuracy of the calibration mixtures has now been stated within section 2.3
- Section 2.2 has been extended in line with helpful suggestions offered by both referees in order to add clarity to the issue of how and when the background levels were recorded for the instrument and chamber and for each experiment. In addition, as suggested by referee #2, the typical variation between background measurements has been quantified and included at this point.
- Following suggestions made by referee #2, the typical hydronium to monohydrate ratios recorded over each experiment have been quoted at the end of section 3.1.
- Also as suggested a typical background mass spectrum has been included in Figure 3 in order to show the clarity of the instrument base line.
- The relevant information regarding weight and power consumption of the CIR-TOF-MS has also been included.

(2) The referee correctly raises the question whether the regression plots in Figure 4 have been forced through zero. Inspection of Figure 4 reveals that this is not the case. Indeed none of the correlation coefficients have been obtained from regression plots which have been forced through zero- a statement has been inserted into section 3.2 to clarify this issue. In addition the slopes for all regression plots are given now in Table 1.

(3) Ethanol - According to Warneke (*et al* 2003), experiments using their standard Ion-icon model PTR-MS indicate that following the proton transfer reaction the protonated ethanol ion will undergo some degree of fragmentation with resultant daughter ions possessing m/z 47, 29 and 19. Clearly, with a mass fragment occupying the same

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channel as the primary reagent ion it becomes very difficult to quantify ethanol using the PTR-MS technique. It is reasonable to expect, that with a higher E/N than Warneke in our custom drift cell (147 Td as opposed to 108 Td) a significantly larger quantity of the protonated ethanol population fragmented to m/z = 19. A statement regarding this issue has been inserted into section 3.1.

(4) In relation to the referee's suggestion as to "good" PTR-MS compounds, the information shown in Table 1 goes someway to answering this question. One of the difficulties with this question is a more fundamental one based on direct mass-spectrometry. What maybe true in one environment may not be true in another, having said that the advantage of multi-channel detection (TOF-MS) is that you do get see a lot including maybe indicators of interferents. The question really merits a good review article.

Minor Comments

(5) Figure 7. The authors have tried a number of colour schemes for this figure and that presented seems to display the data best.

(6) Figure 5. The referee is correct with respect to Figure 5- it does indeed show basic counting statistics. However, the authors felt that it was important to show this in relation to the determination of detection limits.

(7) All figures are now correctly referenced and labelled.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10247, 2006.