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Atmospheric
Chemistry
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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.

Anonymous Referee #2

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This manuscript presents a concise description of the operation and evaluation of a proton transfer - time-of-flight mass spec. during an intercomparison of OVOC methods at the Julich environmental chamber. This is part of the natural evolution of the CIR-TOF-MS technique and is suitable for publication in ACP. The time-of-flight work is very interesting and may provide the motivation for chemical ionization measurement to move away from quadrupoles. I think the authors are moving the field ahead in a unique manner. However, I believe the paper is in need of a few modifications listed below.

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Interactive Discussion

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1) The experimental detail is a little skimpy for a paper that is focused on instrument performance. Two other papers are referenced for the general instrument description but they are not all that detailed. I think inclusion of an instrument schematic is needed unless the instrument is identical to that shown in the 2004 Anal. Chemistry article [Blake et al., 2004]. At least the drift tube should be described in more detail (e.g. composition, size, seals, reaction time) as these parameters may at least influence the background levels of some VOCs. I am not quite sure if the drift tube is more like the standard Ionicon or the more custom “Hanson” type. The accuracy of the calibration mixtures should be at least estimated. How are background levels estimated? How frequently are these tests performed and are they automated? What is the variance between successive background measurements? I would also state the distribution of “reagent ions” (i.e. H3O+(H2O)n) in the experimental section. It would be very helpful to display a “background” mass spectrum to demonstrate which masses are clear of interference and which are more problematic. Finally, giving some idea of the weight and power consumption of the instrument would be very helpful to gain an idea of its portability.

2) Calibration and comparison plots at high levels of analyte (i.e. $>$ a few ppbv) are fine and clearly should be done to demonstrate basic instrument performance. Although it should be stated if the comparison plots (figure 4) have offsets or if they are forced to zero instead of just reporting an R2 dominated by the high mixing ratios. This is very important as most of the species in this study are rarely observed at very high levels in at least the remote atmosphere. For this reason, detection limits for each of the species should be clearly defined. For example, the limit of detection might be defined as some multiple of the variance of the background level. This off course also requires defining the integration time. Once this is done the authors could make a more quantitative statement in the abstract rather than the current “detecting Ě.. down to sub ppbv mixing ratios”. This is vague and I think possibly misleading. I also think the final sentence of the abstract is a little misleading. For example, I am highly doubtful that the method is capable of measuring many of the compounds such as acetaldehyde,

toluene, etc. in a remote environment. Perhaps a more specific statement is needed.

3) The “missing ethanol” is very interesting. This should be expanded upon with at least some potential explanations. Could the ethanol product ion be dissociated and come at the same mass as another species? Do other instruments miss the ethanol?

4) I suggest that the authors give some kind of summary of what compounds they think are going to work the best. This is because as PTR-MS data has become more common in large field campaigns, skepticism about measurements of certain compounds has started to become prevalent in the atmospheric chemistry community. For example, reported acetaldehyde levels are usually ignored because they are so large in the remote atmosphere that they make little sense in relationship to other measurements (HOx, PAN, etc.). Isoprene levels outside of forested areas can be marginal etc. Conversely, acetonitrile seems to be fairly robust as a tracer of biomass burning. I think discussions of this type in the PTR-MS community would be very useful.

Minor stuff:

5) Figure 7 is very difficult to make out. Perhaps another color scheme or background color would be better.

6) As far as I can tell Figure 5 confirms counting statistics and is not that useful.

7) On page 10257, line 25 Figure 5 should be Figure 6- I think. Also some places Fig. is abbreviated and sometime written as Figure.

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

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