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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 #1

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This manuscript describes the performance of a Chemical Ionization - Time of Flight Mass Spectrometer, abbreviated as CIR-TOF-MS, during a large-scale intercomparison project that took place in a 250 m3 FEP chamber. The goal of the project was to perform side-by-side comparisons of instruments capable of detecting oxygenated volatile organic compounds (OVOC). This manuscript only describes the results obtained by the CIR-TOF-MS instrument relative to the calculated concentrations of analyte species expected to be in the chamber. The performance and capabilities of new instrumentation to detect OVOCs at high time resolution and high sensitivity will be of interest to the ACP audience.

However, my overall impression of the current manuscript is that it provides relatively little new scientific or technical value for the readers of ACP that is not already contained in recent publications by the same group elsewhere. It seems to be an extrapolation of ongoing instrument characterization, which is a critical task in the development of new instruments, but not necessarily important for ACP readers to be kept informed of at each step in the process.

The paper does describe results for additional compounds, but similar results for ˜50% of the compounds studied with proton transfer have been described in Blake, 2006. This paper does begin a more quantitative assessment of instrument performance related to atmospheric measurements than previous publications by the group. But, I feel that in its current form the manuscript falls short in this aspect, and could be improved by including information already at hand, and by a change in the format of some of the figures.

Thus, I am somewhat ambivalent about the need for this manuscript to be published in ACP as I feel the most significant new insights regarding CIR-TOF-MS performance will come in its comparison against the other instruments used during the chamber experiments. In the forthcoming manuscript describing the intercomparison, readers will likely be referred to a more detailed description of the CIR-TOF-MS than is provided in the present manuscript under consideration, and section 2.2 of this manuscript will likely be repeated by the forthcoming manuscript. Thus the value of the current manuscript seems uncertain.

If it is to be published in ACP, perhaps a “technical comment” is more appropriate, or the authors need to enhance their discussion of instrument performance as it relates to using CIR-TOF-MS to make actual atmospheric measurements of OVOCs as well as to provide a more detailed description of the instrument configuration and operation during these experiments. I provide some suggestions below.

1. While in the abstract and the introduction, much is made about being able to detect OVOC with high time resolution down to sub ppb levels. However, in the introduction the authors state only that atmospheric concentrations range from parts per tillion to parts per billion. Perhaps a more refined range of concentrations can be given for the OVOC studied in the comparison, i.e. what are typical concentrations in urban areas compared to remote regions.

2. It is hard to discern what the ultimate detection limits of the compounds studied are. I suggest the authors devise an estimate for the detection limit (either time dependent or time independent) and include this in Table 1. For example, the detection limit could be the concentration at which S/N = 2 in a given integration period, or it could be 2-sigma variance in the background, etc. Sensitivity is not the only determining factor for detection in an atmospheric matrix.

3. How often were background spectra recorded and how were background spectra obtained? Was the sample flow pulled through a scrubber of some sort, or was high purity air flooded into the inlet, was it dry or wet, etc? Presumably one could improve upon the uncertainty and variance in the instruments accuracy by taking background spectra often. A background spectrum could be included in Figure 3.

4. Ideally the y-axes in Figures 1 & 4 would be logarithmic (even for the regression plots). Little information about performance at low concentrations can be discerned as is, and this is the region most atmospherically relevant. Granted, concentrations did not span much more than a factor of 10 in these experiments, but deviations at low concentrations are nonetheless apparent even in the current form.

5. The slopes of the regression plots in Figure 4 don't appear to be listed. At least a 1:1 line should be included on each plot. Obviously they are close to 1:1 from visual inspection, but this result is easily quantified. Why not show a correlation plot for one of the species that didn't behave as expected, as opposed to two plots for species that performed nearly equally well?

6. The statement about the effects of O3 needs to be qualified as: “With the sample gas residence time on route to the drift cell of the order of seconds and ozone concentrations less than 60 ppb, ozone/surface effects are expected to be minimal.” The effect of ozone/surface reactions will depend on both the residence time and the O3 concentration, as well as on the exposure of the inlet to unsaturated species. These latter two would likely increase (or decrease in the case of O3) when making atmospheric measurements.

7. The issue of fragmentation of parent ions in the drift tube is a well-known interference in PTR-MS measurements. Here, to assess instrument performance for certain analytes, the contribution of daughter ions from fragmentation had to be removed. The relevance of this step to inferring concentrations measured in an atmospheric matrix are not really discussed. Such contributions won’t be easily removed when the concentration of the parent is itself an unknown.

8. It seems that the intercomparison results will be more instructive regarding the issue of low vapor pressure species detection (or lack thereof). If all the loss is occuring to the chamber walls, all instruments should be biased relative to the predicted concentration. Along this line, could some of the difficulty of detecting formaldehyde be attributed to is loss to surfaces, which likely increases with humidity?

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