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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.

K. P. Wyche et al.

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The referee raises the issue as "to the worth of this paper". One of the critical elements of any technique for measuring atmospheric composition is the performance with respect to specificity and sensitivity. Further than this is the requirement for accuracy and precision. This paper is a cornerstone of the assessment of the performance of an entirely new technique which we hope will help to move PTR-MS/CIR-MS in a positive new direction. Indeed, the authors believe that the submitted paper has great value in its own right as a stand-alone performance assessment of an instrument.

The reviewer is wrong to assert that in the multi-institution paper the "readers will be referred to a more detailed description of the CIR-TOF-MS", the converse will (clearly) be true. In fact only one paragraph in the (potential) multi-institution paper has been allowed for instrument specific experimental information, which *may* be sufficient for some other more mature techniques it is certainly not enough to describe such an instrument as the CIR-TOF-MS.

As the referee correctly points out this work is a technical note. We have received notification from the editor, prior to review informing us that the paper would be reclassified as such. Additionally, following suggestions made by both reviewers, the experimental section has been expanded upon to bring it more in line with the overall nature of the paper, with the inclusion of more detail regarding "instrument configuration and operation".

In reply to the individual points raised

(1) In order to remove a general ambiguity in respect of the time resolution and VOC concentration, an example range of integration times has been added to the final paragraph of the introductory section.

(2) Detection limits. In line with suggestions made by both referees, additional information has been included regarding the determination of absolute detection limits of the CIR-TOF-MS. The method for detection limit calculation has been included along with an additional figure to show how instrument signal/noise ratio varies with compound concentration for a typical OVOC (for, as suggested by the referees, a signal to noise ratio of 2:1).

Owing to calibration limitations the detection limit has been given for a typical example OVOC. In section 3.4 there currently exists a statement regarding the S/N ratios of the test compounds at the lowest concentration measuring period, which gives an indication of the instruments detection limit for the test compounds.

(3) As suggested by both referees, section 2.2 has been extended to provide further

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detail and hence to clarify how, when and how often the instrument and chamber background was measured and how the resultant data were then utilised to provide more accurate OVOC mixing ratios. The authors appreciate, as suggested by referee #1, that the recording of multiple background scans at various points throughout the experiment would improve on accuracy. However, to provide a true background measurement for a chamber experiment the blank scan must been obtained from the chamber air itself and clearly this was possible at only one point during each experiment. The background scan contained the same level of moisture and ozone as in the relevant experiment from which it was subtracted, e.g. dry for experiment 2 and moist for experiments 3 and 4.

Additionally, as suggested by referee #2 (see below), a typical background mass spectrum has been included in Fig 3.

(4) To alleviate the referee's worries with respect to log axes, the full slopes and intercepts have been added to Table 1 and log axes have been added to Figure 5.

(5) Full regression statistics are given in Table 1 for each compound and the values given have been averaged over the three main experiments (2, 3 and 4). The statement on p10257, lines 6 and 7, explains this further. The additional correlation coefficients given with Figure 4 have been quoted for each single respective experiment. For further clarity a final sentence has been added to the caption of Figure 5 starting with *"Correlation (*r^2*) coefficients for each individual experiment: toluene. . . ."*

As noted above in point (4) the slopes of the regression plots have now been added to Table 1. Also as requested by referee #1, a 1:1 line has been included on each of the regression plots in Figure 5 to aid visual quantification of the correlation.

The instances where the correlations and hence accuracy were poor are discussed in detail later in the paper. In addition, Figure 6 attempts to show visually the poor cases and also attempts to explain why such excursions occurred.

(6) The authors agree with the comments made by reviewer #1 in point (6). As such the residence time on route to the instrument has been calculated and included in section 3.3 (Effect of humidity and ozone), along with the suggested statement.

(7) The referee's statement in point (7) is true. However, in this instance only two of the test compounds produced ions in mass channels where interference had to be removed. By altering the drift cell E/N (from the relatively high value of 147 Td used in this work) and through the employ of various other reagent ions (e.g. Wyche *et al.*, 2005), the fragment ion distribution in the mass spectrum can be varied in order to aid compound identification.

(8) The results obtained by other instruments would be constructive in assessing wall loss issues with respect to benzaldehyde and 1-butanol, however at this current stage of instrument development the submitted manuscript is first required i.e. a detailed assessment of basic instrument performance (i.e. a validation against the SAPHIR chamber) before any instrument intercomparison can be performed.

The measurement of formaldehyde using the PTR-MS technique is a special case that requires an entire study of its own and it is not the purpose of this paper to examine this issue, indeed wall loss of formaldehyde could possibly have contributed towards the small measured signal.

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