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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Technical Note: Measuring tropospheric OH and HO_2 by laser-induced fluorescence at low pressure – a comparison of calibration techniques" *by* S. Dusanter et al.

S. Dusanter et al.

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We are grateful to the first anonymous reviewer for his valuable comments. For clarity, the comments are reproduced below with a bold font, followed by our replies. Suggested technical corrections have been done and are not included in the following reply.

12884: "S_{OH} = [OH]*R_{OH}*P_W" R_{OH} can be a function of laser power, dependent if the author does observe such a behavior, it would be more accurate to make a laser power dependent and a laser power independent factor.

To the best of our knowledge, such a laser power dependence has been observed for only one instrument using the FAGE technique (Faloona et al., 2004). However, we agree that this comment must be mentioned in the manuscript and we added the following sentence: "Eq. (1) assumes that R_{OH} is not a function of laser power, as was observed in these studies. However, it must be noted that some previous studies have observed such behavior (Faloona et al., 2004) and care must be taken to determine whether R_{OH} is dependent on laser power."

12885: "However, constant atmospheric O_2 and N_2 mixing ratios as well as the well stabilized internal pressure do not cause variation of the quenching rates." Is the cell pressure actively stabilized or is the change in cell pressure observed under normal operating conditions neglectable? An active stabilization of the cell pressure by variation of the volumetric flow would lead to a variation in the residence time, therefore a change in wall losses and conversion efficiencies HO_2-> OH, which would need a different parameterization.

The cell is not actively stabilized in pressure. The term "stabilized internal pressure" was a bit confusing and has been replaced by "negligible variation of the internal pressure under normal operating conditions."

12891: source of CARULITE or chemical composition.

The manufacturer is Carus Chemical Company. This information has been added in the revised text.

12892: "The monitor is calibrated against a photometric O_3 calibrator (API, M401) and the uncertainty of the measurement is estimated to 0.5 ppb at the detection limit." What is the detection limit of the O_3 monitor?

During calibration experiments, the O_3 measurements were averaged over 5-min in order to improve the detection limit to better than 0.1 ppb. This has been added in the revised manuscript.

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12894: "Although the overall intensity of the lamp decreased as the cooling flow was increased, measurements of O_2 were independent of the cooling flow, suggesting that the oxygen absorption cross section measured for the mercury lamp used during these OH calibrations is not dependent on the lamp temperature." What was the range of observed lamp temperatures? Can a general statement of the temperature dependence of the line width be made, is it even necessary or would a to the actual temperature range limited statement be sufficient?

Unfortunately, the lamp temperature was not measured during this study. The goal of changing the cooling flow for this particular mercury lamp was just to rule out potential variations of σO_2 during the course of these calibration experiments. Although we believe that the changes in the lamp temperature probably covered the range of temperature we could encounter in the field, a general statement cannot be made. Additional rigorous tests must be performed to check the lamp temperature variations during field measurements in order to reproduce them during laboratory experiments. In addition, some lamps may exhibit a different behavior than the specific mercury lamp we used in this study.

12900: This ratio (C_{HO2}) is closed to unity and suggests a high conversion efficiency. How close is close? 90%, 99.99%?

The conversion efficiency was mentioned in Table 2 as 1.02 $\pm$ 0.07 (1 sigma). It has been added in the text of the revised manuscript. We are aware that the HO_2 conversion into OH cannot be unity, and taking into account the uncertainty on the measurements, the most realistic value lies certainly in the lower range of the determination (eg. approximately 95%). This has been added in the revised manuscript.

12901: "The laser-generated OH is detected within the same laser pulse that produced it. The current set-up of the IU-FAGE instrument was found to be sensitive to this interference under the high concentrations of O_3 used in these calibrations, probably because of beam overlapping in the multi-reflection White cell."

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Could it be also a recirculation of a fraction of sample air within the detection cell? Does the addition of C_3F_6 removes the signal? The term "laser generated signal" used throughout the paper is sufficient to explain the effect.

As pointed out in this comment, a fraction of the detected laser generated OH may be due to recirculation of a previously probed air mass. Unfortunately, the C_3F_6 test mentioned above was not implemented during these calibrations and we do not have useful information to resolve this point. It is worth noting that this does not invalidate the way we treated the laser generated OH during O_3-alkene calibrations. However, this is an important point to resolve for field measurements and further work will be performed on the IU-FAGE instrument to resolve this issue.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 12877, 2007.

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