

***Interactive comment on* “Technical Note:  
Measuring tropospheric OH and HO<sub>2</sub> by  
laser-induced fluorescence at low pressure – a  
comparison of calibration techniques” by  
S. Dusanter et al.**

**Anonymous Referee #1**

Received and published: 30 October 2007

General Comments The in situ instruments to measure OH have developed in the last two decades to a level where the biggest uncertainty remains the absolute calibration. Due to its simplicity and apparent robustness the calibration method based on water photolysis at 184.9nm became the most wide spread method to calibrate OH instruments. One problem with having one commonly used method is that principle uncertainties may still remain uncovered until the calibration technique is compared to a completely different method. This well written technical note compares the wide spread method of water photolysis with a completely different approach based on a

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steady state concentration of OH generated by O<sub>3</sub>+alkene (T2B) reaction. Due to its importance not only for the groups working on OH measurements but also for the whole community using OH measurements, I recommend the publication after minor revisions.

#### Specific Comments / Technical corrections

12883 : something seems to go wrong in the formatting of Q13 (Q1 Eq(3))

12884 : "SOH = [OH]\*ROH\*PW" ROH 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.

12885 : "However, constant atmospheric O<sub>2</sub> and N<sub>2</sub> 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<sub>2</sub>->OH, which would need a different parameterization.

12891 : source of CARULITE or chemical composition

12892 : "The monitor is calibrated against a photometric O<sub>3</sub> calibrator (API, M401) and the uncertainty of the measurement is estimated to  $\pm 0.5$  ppb (1) at the detection limit." What is the detection limit of the O<sub>3</sub> monitor ?

12894 : "Although the overall intensity of the lamp decreased as the cooling flow was increased, measurements of O<sub>2</sub> 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

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range limited statement be sufficient ?

12900: "This ratio ( $\text{CHO}_2$ ) is closed to unity and suggests a high conversion efficiency."  
How close is close ? 90 %, 99.99% ?

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 20 under the high concentrations of  $\text{O}_3$  used in these calibrations, probably because of beam overlapping in the multi-reflection White cell." Could it be also a recirculation of a fraction of sample air within the detection cell ? Does the addition of  $\text{C}_3\text{F}_6$  removes the signal ? The term 'laser generated signal' used throughout the paper is sufficient to explain the effect.

12926 : "<<symbol>> 2.4 ppm  $\text{O}_3$ " the diamond in the caption should be filled grey.

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

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