

Interactive
Comment

***Interactive comment on “Technical Note:
Measuring tropospheric OH and HO₂ 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 second reviewer for the detailed comments and suggestions which helped us to improve the manuscript. For clarity, the comments are reproduced below with a bold font, followed by our replies. Suggested technical corrections have been included in the revised manuscript and are not included in the following reply.

Page 12878 Abstract. The experimental uncertainties of both techniques should be given, and also the % agreement between the two. It should also be explicitly stated that 2 actinometric methods were used to determine the product $F \times t$ necessary for the H₂O photolytic method, and the level of agreement between

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these 2 methods stated. It should also be made clear when giving the agreement between the H_2O photolytic and the O_3 /alkene techniques, which actinometer this corresponds to (assume this is O_2 actinometry as the most commonly used field calibrations).

We agree that this information is useful in the abstract and it has been added to the revised manuscript.

Page 12880 A third useful exercise is to use the same calibration set-up, and to use it on different field instruments (i.e. from different institutes). Differences in inlet design and flow requirements may make this difficult though, unless some -standard- flow or inlet is agreed by the community. It could be worth adding this to (i) and (ii).

We added this point in the introduction section as well as a reference for the study performed by X. Ren and coworkers (Ren et al., 2003). This study involved a FAGE and a CIMS instrument which were deployed to measure HO_2 at a rural site. Both instruments were compared by exchanging calibration sources and an excellent agreement was observed in the HO_2 calibration comparison.

Page 12884, line 25. When discussing HO_2 calibration, it might be worth mentioning the advantages of CO addition, which is used by some other workers to obtain the absolute sensitivity of HO_2 (R_{HO_2}) without having to calculate a conversion efficiency (C_{HO_2}).

This point has been added in the experimental section as follows: "It is worth mentioning that R_{HO_2} can be directly determined using the addition of CO inside the calibrator (not used in this study) before irradiation in order to convert OH into HO_2 in the calibration system (Kanaya et al., 2001)."

Page 12885, line 17: How is the laser power monitored?

The laser power is monitored using two photodiodes equipped with interference filters

at 308-nm at the exit of the dye laser and at the exit of the White cell. This information has been added to the revised manuscript.

Page 12887: The range of OH used in the calibration source is in the 10^9 to 10^{10} region. This is 3-4 orders of magnitude higher than ambient levels. Although multipoint [OH] calibrations enable one to see that the signal is linear with laser power, it would be advantageous to perform calibrations at lower concentrations to check that the slope is the same there. Perhaps a comment on this could be added.

We agree that OH instruments should be calibrated at OH concentrations similar to what observed in the atmosphere and our calibrator will be improved in order to do so. However, we added a figure (Fig. 6) displaying the measured OH signal as a function of the OH concentration. The signal has been corrected for the water-vapor quenching effect which usually increases with increasing OH concentrations due to the use of higher mixing ratios of water-vapor. A linear regression between the corrected signals and the OH concentrations shows the excellent linearity of the detector response and the negligible intercept observed confirms that this instrument can be calibrated with OH concentrations up to 3-4 orders of magnitudes higher than ambient levels.

Page 12890. Although a minor channel, there is also the quenching of $O(^1D)$ by N_2O to give $O(^3P)$.

This comment has been added to the revised manuscript.

Page 12891. Who is the manufacturer or supplier of CARULITE?

The manufacturer is Carus Chemical Company. This information has been added to the revised manuscript.

Page 12892. What is the detection limit of the Teledyne O_3 monitor? The uncertainty is plus/minus 0.5 ppb at the detection limit (which is?)

This question has been addressed in the reply to the first reviewer.

Page 12893, line 13: Was all the 254 nm light filtered out when the oxygen cross section experiments were performed? Would some absorption of 254 nm by e.g. O₃ affect the results at all, affecting the agreement between $F \times t$ calculated using the two actinometry approaches?

As discussed in the manuscript, care was taken to filter the 254-nm emission line during oxygen absorption cross section measurements. Two interference filters were used to isolate the 184.9-nm emissions. Moreover, a flow of air containing N₂O (which exhibits an absorption cross section 4 orders of magnitude lower at 254-nm than at 184.9-nm) was used to confirm that all the photons at 254-nm were filtered out.

The much larger wall loss here compared to Faloona, this shows how important it is to measure the OH decay down the calibration flow-tube for every individual set-up to prevent errors.

We agree with this comment and it has been added to the revised manuscript.

The conversion efficiency (C_{HO_2}) cannot be unity, because of OH+NO+M giving HONO+M. What is -close- to unity? Was the additional signal due to HO₂ conversion compared with an HO₂ only source (with the addition of CO?)

The first question has been addressed in the reply to the first reviewer. Unfortunately, as the focus of this paper was on the comparison of R_{OH} from two different techniques, the addition of CO was not used during these calibration experiments to characterize R_{HO_2} .

What is the detection limit of the NOx analyser towards NO and NO₂?

The NOx measurements were averaged over 5-10 minutes and the detection limit was better than 0.4 ppb. This information has been added to the revised manuscript.

Is a further comment required on the factor of 1.3 to 1.5 difference between the two actinometer methods? Which method is considered the best?

In light of the comments of R. Commane, it appears that the JPL recommendation includes recent measurements of the rate constants for the $\text{O}(^1\text{D})+\text{N}_2\text{O}$ and $\text{O}(^1\text{D})+\text{N}_2$ reactions. The text in the manuscript has been rephrased as the following: "A comparison between both techniques shows that the N_2O photolysis approach leads to a value for $(F \times t)$ that is consistently above the O_2 photolysis method by a factor 1.5 when $(F \times t)$ is derived from the most recent recommendations for k_{15} and k_{16} by Sander et al. (2006). Interestingly, using the rate constants recommended by Atkinson et al. (2004) lead to better agreement (factor 1.3) between the techniques compared to the more recent recommendations. Additional measurements are needed to resolve the discrepancy between the two techniques."

The following sentences have also been added to the revised manuscript: "However, this difference is within the uncertainties stated in Table 2, and these results give confidence in the characterization of the photon flux and the photolysis time performed with O_2 actinometry during OH calibrations. Use of this method is preferred over the N_2O technique for several reasons. The former is more precise because no kinetic parameters are involved in the determination of $(F \times t)$. In addition, the latter technique require a correction of $(F \times t)$ due to the strong absorption of N_2O at 184.9-nm.

How it is known that improving the laser alignment in the multipass cell will allow calibration in dry air?

The statement about decreasing the laser generated OH by improving the laser alignment was a bit confusing. As stated in the manuscript, we believe that the laser generated OH is due to beam overlapping inside the multipass cell. We have added the following clarification to the revised manuscript: "Minimizing beam overlap through improvement of the beam alignment in the multi-pass cell and a reduction in the beam diameter should minimize the laser generated OH and allow calibration of the IU-FAGE instrument in dry air."

Is the 40% difference in the two techniques for the same humidity? Also, which of

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the two actinometer methods for H₂O photolysis technique does this correspond to? Assume it refers to O₂ actinometer, but should be stated clearly.

40% is an approximate average for the differences observed between R_{OH} extrapolated for dry air conditions (43%) and R_{OH} measured at 0.5% water (38%). The revised manuscript has been rewritten to clarify that O₂ actinometry was used to during water-vapor UV-photolysis calibrations.

R_{OH} is expected to decrease by 13% per percent of water vapour for both methods; presumably due to fluorescence quenching? Say this to be clear.

This has been clarified in the revised manuscript.

Page 12909, line 25: Final sentence is confusing. It is true that the uncertainty in the O₃/alkene technique is considerable (and it is difficult to give the exact uncertainty due to gaps in the knowledge of the reaction mechanism and kinetic parameters); and the fact that the H₂O photolysis technique agrees within 40% means that it cannot be too much in error. However, although this level of agreement may provide some confidence in the H₂O photolysis method, it is more difficult to say that it implies the H₂O photolysis method is accurate, as the O₃/alkene method may be subject to large uncertainties, and 40% away from something that is a long way off is still some way off! However, this level of agreement between two methods does increase the overall confidence with calibration.

We agree that the last sentence is a bit confusing. It has been rephrased as the following: "However, the level of agreement observed between these two different methods improves the confidence of the water-vapor photolysis method as an accurate calibration technique for HOx instruments."

12917 Table 2. Can the H₂O vapour photolysis method generate lower concentrations of OH? 0.1-0.55% water vapour is low compared to the majority of ambient

conditions (1-2%) which can be up to 3-4% in hot, humid conditions.

Yes, the water-vapor photolysis technique can be used to produce lower OH concentrations, even at higher water-vapor mixing ratios than displayed in Fig. 6 (now called Fig. 7 in the revised manuscript). It is relatively easy to generate humid air with water-vapor mixing ratios up to 2% when the total flow rate does not exceed 10 SLPM. However, in order to reach absolute water mixing ratios of 2-3% at a total flow rate of 50 SLPM, the water-vapor saturation system used in our calibration system needs to be improved.

The OH concentration generated within the calibrator depends on the intensity of the lamp emission at 184.9-nm. The minimum flux used in our system depends on the feasibility to accurately measure the low O₃ concentrations generated. This limitation can be overcome by further improvement of the calibrator. The relative intensity of the flux at 184.9-nm can be measured by a photodiode located on the opposite side of the calibrator with regards to the lamp module. It has been shown by other authors (Holland et al., 2003) that a linear relationship can be determined between the photodiode signal and the amount of O₃ produced inside the calibrator. This relationship is determined for O₃ mixing ratios generated above the detection limit of the ozone monitor. When this relation is established, the lamp flux can be decreased (below measurable O₃ concentrations) and the signal measured allows extrapolating the amount of O₃ produced within the calibrator.

Our calibrator system is being modified to meet the two requirements mentioned above in order to generate low concentrations of OH under high water-vapor mixing ratios.

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