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Atmospheric
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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 R. Commane for these helpful comments. For clarity, the comments are reproduced below with a bold font, followed by our replies

The recommended IUPAC rates (Atkinson et al 2004) (used to determine the lamp flux from N_2O actinometry) do not include recently updated rates for $O(^1D)$ + N_2 and $O(^1D)$ + N_2O, which are included in the JPL evaluation (Sander et al 2006). From this, the lamp flux calculated using the JPL rate equations could be considered more appropriate than that calculated using IUPAC rate equations, suggesting the agreement factor between the actinometric methods of 1.5 is more

accurate.

We thank R. Commane for bringing this information to our attention. The discussion about the difference observed between the two actinometric techniques has been modified as the following: "A comparison between both techniques shows that the N_2O photolysis approach leads to a value for (F × t) that is consistently above the O_2 photolysis method by a factor 1.5 when (F × 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. However, this difference is within the uncertainties stated in Table 2, and gives confidence in the characterization of the photon flux and the photolysis time performed with O_2 actinometry during OH calibrations."

These calibrations are carried out at a concentration much higher than ambient OH concentrations. A sensitivity plot of the signal recorded for a given OH concentration would prove useful. Is the sensitivity linear over all concentrations calibrated for? Is there an intercept present if this linear relationship is extrapolated to zero? Using a FAGE instrument and similar wand-type calibration system, I have found that the instrument sensitivity at the high OH concentrations used here is not consistent with that determined from near ambient concentrations of OH.

This comment has also been addressed for reviewer 2. A plot exhibiting the dependence of the measured OH signal (corrected from the water-vapor quenching effect) towards the OH concentration sampled by the IU-FAGE instrument has been included in the revised manuscript (Fig. 6). The relationship between the two quantities mentioned above shows that the detector response is linear with the OH concentration and the negligible intercept observed confirms that this instrument can be calibrated with OH concentrations higher than ambient levels by 3 to 4 orders of magnitudes. In addition, the signal linearity has also been observed over a large range of OH concentrations (10^6-10^{12} cm^{-3}) by other authors (Stevens et al., 1994; Holland et al., 1995; Kanaya et al., 2001).

Figure 5 shows the minimum distance from OH production to sampling of 9 cm. Why is the sampling point located so far from the the site of OH production? How much internal (within the wand) and external (open to lab air) distance prior to sampling does this include?

The minimum distance between the site of HOx production and the exit of the wand depends on constraints due to the calibrator design. Fig. 2 was not drawn to scale and it has been modified to better represent the actual dimensions of the calibrator. The lamp module, designed to be movable along the calibrator length, is 10-cm long and the HOx production occurs at the center (5-cm from the left part of the module in Fig. 2). In addition, in the present design this module cannot be moved directly adjacent to the exit of the wand (at best 3-cm from the exit). As a consequence, the minimum distance between the HOx production point and the wand exit is 8-cm. At the minimum distance, this implies that the air mass containing the radicals must go through 8-cm of the wand. However, the loss of radicals occurring along the calibrator is assessed by extrapolating the measured signal as shown in Fig. 5.

For the calibration experiments presented in this paper, the calibrator was interfaced to the IU-FAGE instrument with an "open to lab air" distance of approximately 0.5-cm. Tests were performed to check the sensitivity of the OH signal when moving the calibrator away from the nozzle. It appeared that the OH signal was constant when the "open to lab air" distance was varied between 0.5 and 4-cm. This insensitivity of the recorded signal is an advantage of using a flow rate through the calibrator (50 SLPM) which is five times higher than the required sampling flow rate (9-10 SLPM).

Is the power supply to the mercury lamp maintained at a constant voltage during the calibrations?

The lamp current is maintained at a constant voltage during a calibration experiment (when the lamp module is adjusted over the wand length to characterize the loss of radicals at constant concentrations of OH and HO_2). During the course of the experiments, the voltage was varied to produce various concentrations of OH for a given water-vapor mixing ratio. This can be done because the characterization of the lamp flux at 184.9-nm shown that the oxygen absorption cross-section was independent on the operating conditions.

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