

***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 #2**

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General Comments

The measurement of OH and HO<sub>2</sub> radicals in the atmosphere using laser-induced fluorescence spectroscopy is only quantitative if the relationship between the observed signal and the OH (or HO<sub>2</sub>) concentration can be established. The reliability and accuracy of the calibration is what determines the quality of the measurements. This technical note compares two calibration techniques. The first uses two different actinometric methods for calibrating the product of the 185 nm flux and photolysis time ( $f \times t$ ) that is used for the photodissociation of water vapour (in a turbulent tube) to give OH

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and HO<sub>2</sub> (in the presence of O<sub>2</sub>) radicals. This is a widely used technique, once the flux is known the OH can be calculated from [H<sub>2</sub>O]. An alternative method is to obtain the absolute flux F (not used in this paper) using a photodiode or other light sensor that has been absolutely calibrated versus a National Standard. The other (distinct) calibration technique described in this work utilises the reaction of ozone with an alkene (T2B) whose products include OH.

Field measurements of OH and HO<sub>2</sub> have matured, there are several methods (FAGE, DOAS, CIMS) that are sufficiently sensitive to measure OH in the field without significant interferences, and the focus now is less on instrumental details, and more on the comparisons between the field measurements and the model comparisons. However, as discussed in this paper, there remain some uncertainties in the calibration methods, which limit the confidence of the conclusions that are gained from comparison between model and experiment. I applaud this technical note, which is the result of some careful and detailed experiments, and provides a critical account of two very different techniques. Although both techniques have been used to calibrate field measurements in the past (but the O<sub>3</sub>/alkene only very rarely), this paper represents the first detailed comparison of the two, and is a timely technical note. Some new insights have emerged from the comparison, with important implications for the field measurement of HO<sub>x</sub>.

The overall conclusion is that the two calibration techniques do not agree particularly well (40%), although the agreement is within their combined error bars. The O<sub>3</sub>/alkene technique has not really enjoyed a wide application for the calibration of field instruments, but its development is very important, as currently virtually all the HO<sub>x</sub> data in the literature rely on the other technique (H<sub>2</sub>O photolysis), which is a very dangerous state of affairs. There have been examples of changes in absorption cross-sections (e.g. O<sub>2</sub>) or unexpected changes in the absolute sensitivity of light sensors, which have brought into question the accuracy of some previous data and prompted reinterpretation of data.

However, there are good reasons given in the paper for expecting some disagreement

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between the two techniques that are compared in this work. The O<sub>3</sub>/alkene method relies more heavily on rate coefficients and product branching ratios (for OH) that are not well established, or which change with different experimental conditions. For example, the yield of OH from O<sub>3</sub> + T2B is thought to be time dependent. The values in the literature (called global yields and used here in the calculation of OH), are usually obtained in smog-chamber experiments with long reaction times, whereas the experiments here uses a shorter reaction time to generate OH, for which the yield is not known, but is probably lower than the global yield. It is also possible that some of the intermediates in the O<sub>3</sub>/alkene system, for example Criegee intermediates, may decompose via unquantified pathways to form OH, and that yields may be humidity dependent. Also, the O<sub>3</sub>/alkene technique uses ppm levels of O<sub>3</sub>, and in the presence of water vapour (which needs to be present if calibration under realistic ambient conditions are to be performed) generates significant quantities of artefact OH, which needs to be subtracted, leading to increased uncertainties.

Despite the possible complications of the O<sub>3</sub>/alkene method, the agreement with the H<sub>2</sub>O/actinometric method is close enough to provide increased confidence with the use of the latter in the field. However, the two actinometer methods (O<sub>2</sub> or N<sub>2</sub>O) to determine the product of (flux x photolysis time, F<sub>xt</sub>) disagree by a factor of 1.3 or 1.5, depending on which of the evaluated databases (Atkinson or Sander) is used. Although this is within the combined uncertainty; it shows that further work is still required to provide a better measurement of the product F<sub>xt</sub>. The authors conclude that caution is need in the use of the O<sub>3</sub>/alkene method, but hat after some further work in the laboratory to establish time dependent OH yields, and to unravel some other details of the mechanism, this method may become more useful in the future.

I strongly favour publication in ACP as a Technical Note. The paper is well written, and the methodology is very good, and represents a significant advance in the development of methods for the calibration of HO<sub>x</sub> field instrumentation. Table 1 is a useful resource. It shows that there is still quite a bit of work to be done on calibration methods.

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Specific comments/technical corrections.

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  $F_{xt}$  necessary for the H<sub>2</sub>O photolytic method, and the level of agreement between these 2 methods stated. It should also be made clear when giving the agreement between the H<sub>2</sub>O photolytic and the O<sub>3</sub>/alkene techniques, which actinometer this corresponds to (assume this is O<sub>2</sub> actinometry as the most commonly used field calibrations).

In situ rather than in-situ (other places also)

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).

Page 12883. Formatting , Eq(3) keeps appearing after the Q1 for some reason. Eq(1) later. Also on some other pages.

Page 12884, line 25. When discussing HO<sub>2</sub> 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<sub>2</sub> (RHO<sub>2</sub>) without having to calculate a conversion efficiency (CHO<sub>2</sub>).

Page 12885, line 17: How is the laser power monitored? Next line extra comma not needed.

Page 12887 The range of OH used in the calibration source is in the 10<sup>(9)</sup> to 10<sup>(10)</sup> 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.

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Page 12888 Open bracket before Schultz,

Page 12890. Although a minor channel, there is also the quenching of O(1D) by N<sub>2</sub>O to give O(3P).

There is also a discussion of using both O<sub>2</sub> and N<sub>2</sub>O actinometry to determine the product Fxt, under laminar and turbulent flowtubes, in Whalley et al (2007), J. Atm. Chem., for calibrating a similar FAGE instrument, but to measure IO radicals.

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

Page 12892. What is the detection limit of the Teledyne O<sub>3</sub> monitor? The uncertainty is plus/minus 0.5 ppb at the detection limit (which is?)

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. O<sub>3</sub> affect the results at all, affecting the agreement between Fxt calculated using the two actinometry approaches?

12899 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.

12900 The conversion efficiency (CHO<sub>2</sub>) cannot be unity, because of OH+NO+M giving HONO+M. What is -close- to unity? Was the additional signal due to HO<sub>2</sub> conversion compared with an HO<sub>2</sub> only source (with the addition of CO?)

12900 Line 2 -close- not -closed- Line 5- separate and not separated What is the detection limit of the NO<sub>x</sub> analyser towards NO and NO<sub>2</sub>? 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?

12902 Cannot rather than can not How it is known that improving the laser alignment in the multipass cell will allow calibration in dry air?

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12904 A good point is made that the O<sub>3</sub>/alkene technique will not work with the CIMS method where H<sub>2</sub>SO<sub>4</sub> is generated.

Is the 40% difference in the two techniques for the same humidity? Also, which of the two actinometer methods for H<sub>2</sub>O photolysis technique does this correspond to? Assume it refers to O<sub>2</sub> actinometer, but should be stated clearly.

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

Page 12909, line 25: Final sentence is confusing. It is true that the uncertainty in the O<sub>3</sub>/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 H<sub>2</sub>O 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 H<sub>2</sub>O photolysis method, it is more difficult to say that it implies the H<sub>2</sub>O photolysis method is accurate, as the O<sub>3</sub>/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.

12917 Table 2. Can the H<sub>2</sub>O 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.

It is interesting that the uncertainty changes quite a bit depending on whether Atkinson (2004) or Sander (2006) is used.

Using CO to convert OH to HO<sub>2</sub> prior to the pinhole would eliminate one term in the uncertainty, namely C(HO<sub>2</sub>).

12918 Table 3. Can the OH concentration also be given in this table to be consistent

with Table 2?

12921 Figure 3. Can a comment be made to explain the wide range of cross-section values at the typical O<sub>2</sub> column density of  $6.1 \times 10^{18}$  molecule cm<sup>-3</sup>? This is just the range obtained when the current and voltages of the lamp are changed?

12924. Fig 6.

12926 Figure 8, caption, it is a grey diamond.

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

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