

Interactive comment on “Validation of the calibration of a laser-induced fluorescence instrument for the measurement of OH radicals in the atmosphere” by W. J. Bloss et al.

W. J. Bloss et al.

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Response to reviewer comments

The authors wish to thank two anonymous referees for their comments on the manuscript; responses to the specific points mentioned (paraphrased below), and details of modifications to the manuscript, are given below.

Referee #1

Comment: Mixing ratio units for background NMHC measurements in the chambers would be preferable to the mass per unit volume figure given.

Response: The concentration of NMHC in the "empty" chamber ($\text{NMHC} \leq 0.3 \text{ ug/m}^3$) is obtained from mass measurements of hydrocarbon scrubbing filters. Assuming a

mean molecular mass of 114 (octane) for urban Valencia air, this is equivalent to a mixing ratio of 60 pptv: We have therefore changed the manuscript to quote a conservative upper limit to the background chamber NMHC mixing ratio of 0.2 ppbv.

Comment: Upper limit of 200 ppmv for NO_y in the background chamber is not very low; what were initial hydrocarbon / NO_x levels employed in the experiments ?

Response: The figure of 200 ppmv in the manuscript refers to H₂O only: NO_y levels in the background "empty" chamber prior to admission of any reactants are much lower (< 1 ppbv). We have changed the manuscript to clarify this point. This upper limit for background NO_y can be compared to initial NO_x levels added to the chamber at the start of experiments, ranging from 40 to 500 ppbv. Table 2 has been revised to give the initial NO_x and hydrocarbon mixing ratios employed.

Comment: What were the differences between the repeated toluene and benzene experiments ?

Response: The two Toluene experiments were performed with different initial NO_x levels as indicated in the revised Table 2: 509 and 150 ppbv for experiments 1 and 3 respectively - selected in order to perform experiments in both the VOC- and NO_x-limited regimes for the purposes of validation of the toluene degradation mechanism in the Master Chemical Mechanism (Pilling, 2003). Similarly the two benzene experiments, Nos 7 and 8, differed in the initial NO_x:VOC ratios used.

Comment: Might renumbering the experiments, so that those performed upon similar chemical systems are grouped together, make sense ?

Response: The numbering scheme adopted in the paper is chronological - we feel that this scheme is more useful than grouping experiments performed upon the same principal hydrocarbon species, as the emphasis of the present work is upon the inferred OH concentrations, rather than the hydrocarbon photo-oxidation chemistry. The chronological position of the experiments relative to the calibrations and to each other

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are relevant to the discussion of the agreement (or otherwise) between the LIF and HC derived OH measurements - as they indicate that no drifts in the system calibration occurred. The text refers to the repeated experiments on pages 6044 and 6048, and in the caption to table 2.

Comment: What is the statistical uncertainty in the FTIR measurements, and its contribution to the value of R ($= [\text{OH}]\text{LIF} / [\text{OH}]\text{HC}$) for each system ?

Response: The estimated statistical (random) uncertainty in the FTIR and HPLC measurements are 2 % and 4 % respectively. This point-to-point uncertainty will contribute to scatter in the retrieved hydrocarbon concentrations, and hence the inferred OH concentrations, but will not impart a systematic change to the value of R . We have modified the manuscript (p.6047, discussion of uncertainties in the FTIR data) to mention and quantify this contribution to the uncertainty in R .

Comment: What other factors could be responsible for artefact signals or errors in the retrieved $[\text{OH}]\text{LIF}$? A squared dependence upon laser power would indicate an artefact signal. Are similar discrepancies observed for other hydrocarbons ?

Response: We agree that a squared-laser-power dependence to the LIF signal in the 1,3,5-TMB experiments would be an excellent indicator of a photolytic artefact signal; unfortunately during the experiment laser power was not varied systematically in this way (the experiments were not fully analysed in real time, so the discrepancy was not identified until after the end of the campaign - we intend to modify the experiment protocol in future to ensure such tests are carried out). The fluorescence cell construction is such that the gas flow through the nozzle experiences smooth increases in diameter of the LIF cell until the final diameter (70 mm) is achieved, over a distance of approximately 100 mm, with the windows to the optical axes positioned approximately 50 mm from the LIF region so few possibilities for unflushed space exist; the gas flow rate through the expansion ensures that each laser pulse impinges upon a fresh volume of sampled air. The $[\text{OH}]$ observed by the LIF was below detection limit

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(ca. $1e6$) molecules cm^{-3} after the addition of 1,3,5-TMB and prior to the opening of the chamber, and fell to $< 1.5e6$ molecule cm^{-3} immediately the chamber was closed, so if surface reactions were contributing to an artefact signal, they are unlikely to have involved either 1,3,5-TMB or the stable products of its photo-oxidation. We have observed surface effects in much larger LIF cells, without shielding curtain flows, at the University of Leeds, following exposure of the cells to high concentrations of NO, but such signals were immediately apparent and lasted for a period of several days. In the case of the 1,3,5-TMB system, GC-FID results indicate that the concentrations of 1,3,5-TMB retrieved from the FTIR spectra may be overestimates at long times (low 1,3,5-TMB levels) - this would result in underestimated [OH]HC at later times in the experiment, and hence to an overestimate of R. We have modified the manuscript (p. 6047, 6049) to discuss this possibility in greater detail. With regard to comparison with other measurements, we are not aware of any analyses similar to the current work performed upon the same aromatic species for comparison - however future experiments at EUPHORE, and other environmental chambers such as SAPHIR, may elucidate causes of discrepancies such as that observed for the 1,3,5-TMB system.

Referee #2

Comment: Presentation of the calibration uncertainty would be improved by indicating the overall uncertainty in Table 1

Response: We have modified the table to clearly indicate the overall uncertainty, in addition to the individual components, as suggested.

Comment: It would be informative to give the initial overall NO_x levels for each experiment.

Response: Table 2 has been modified to include the initial VOC and NO_x mixing ratios, in line with the comments of referee 1 also.

Comment: What is the purpose of the measurement of scattered solar radiation, during

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a second photon counting window tens of microseconds after each LIF pulse ?

Response: The scattered solar radiation is measured, in order that its contribution to the measured signal may be subtracted. The measured signal during the first acquisition interval, immediately after the laser pulse, contains contributions from OH LIF, some scattered laser light, solar scatter and detector dark noise. The second acquisition window described allows subtraction of the solar scatter (and incidentally detector dark current). The contribution from scattered laser light is determined through the off-line measurements, which are performed approximately every 90 seconds. The contribution from scattered solar light is accounted for in this manner, through the use of the second acquisition window, rather than via the off-line measurement, in order to avoid errors due to variations in solar intensity between the on-line and off-line measurements - due to the sun passing behind a cloud, or the framework supporting the reactor chamber, for example. We have added a line to the manuscript (page 6033, line 14) to clarify this point.

Comment: The dimensions of the flow tube are such that the flow is not strictly laminar at the LIF nozzle.

Response: We agree that while the Reynolds number for the flow within the tube (approx. 1500) is in the laminar regime, the tube length is not sufficient for fully laminar flow to have developed at the point where the flow passes the mercury lamp / impinges on the nozzle - a characteristic length of approximately 100 cm is required for flow to be within 5% of its maximum laminar (poiseuille) value, which may be compared with a tube length used of 60 cm. We have added a qualification to the manuscript on this point. The difference should however not affect the analysis, as the profile factor (P) is measured under the actual conditions (flow tube dimensions, flow rates etc.) of the measurements, and so incorporates the extent to which radial turbulent mixing is occurring.

Comment: The abbreviation "slm" needs to be defined in the paper.

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Response: We have modified the manuscript to define "slm" as standard litres per minute on p. 6034.

Comment: Please give references for the quantum yields for production of OH / O₃ arising from H₂O / O₂ photolysis.

Response: References for the quantum yields for OH and O₃ production upon photolysis of H₂O and O₂ (respectively) at 184.9 nm have been added (Sander et al., 2003 and Washida et al., 1971).

Comment: What is the uncertainty in the FTIR measurements, and its contribution to the uncertainty in the value of R ?

Response: Uncertainty in the FTIR / HPLC measurements: See response to Referee 1's remarks, above.

Comment: 1,3,5-TMB needs to be defined at first appearance.

Response: We have modified the manuscript to define TMB as trimethylbenzene on p. 6044.

Comment: Please quantify the agreement between the FTIR and GC-FID measurements of 1,3,5-TMB.

Response: The FTIR and GC-FID derived 1,3,5-TMB measurements agreed to within better than 1 % for mixing ratios greater than 75 ppbv (the experiment started with 275 ppbv of 1,3,5 TMB). At lower mixing ratios (later times) the FTIR concentrations were higher than those from the GC-FID, by up to 15 ppbv - equivalent to 50% at the end of the experiment - possibly indicating that the FTIR retrieval of 1,3,5-TMB concentrations was being affected by (for example) an overlapping product spectrum, as considered on page 6047 of the manuscript. We have amended the manuscript to quantify (and comment on) the FTIR / GC-FID comparison.

Comment: Please verify the OH number density value - should this be 14000 cm⁻³,

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rather than the 17000 cm⁻³ given on page 6048 ?

Response: The calculation of the OH number density inside the FAGE cell used a pressure of 1.6 mbar, as given on p. 6033, and a temperature of 220 K (this is the OH rotational temperature obtained from a Boltzmann analysis of the relative intensities of different OH transitions within the (0,0) band). This temperature is mentioned in the manuscript on page 6036, however it is possible, or indeed likely, that both temperature and pressure exhibit strong gradients within the LIF cell - thus the calculated number densities should only be regarded as approximate; we have clarified the origin of the values given on p. 6048 of the manuscript. The discrepancy noted by the referee arises from the use of 220K rather than 300 K in the calculation of [M]. The point arising from the number density calculations - that the OH concentration within the cell arising from sampling of ambient chamber OH is orders of magnitude much higher than that which could arise from the photolysis of methyl glyoxal, PAN or HCHO - is valid irrespective of whether 220 K or 300 K is used.

Comment: What other possibilities, or combination of factors, may give rise to OH artefact signals - could Criegee decomposition or photolysis within the LIF cell contribute to the returned [OH]LIF ?

Response: Other LIF artefacts: Surface effects and the possibility of checking for photolytic artefacts by varying laser power are discussed above (response to referee 1 comments). Excited Criegee species are known to decompose to yield OH radicals, which could contribute to errors in the LIF measurements; while their stability might be expected to be enhanced in the low temperature gas expansion, the reduced pressure in the LIF cell might increase the quantum yield for OH formation via their decomposition, as the rate of collisional stabilisation will be lowered. However the aromatic hydrocarbons do not react with ozone at an appreciable rate: $k(1,3,5\text{-TMB} + \text{O}_3) < 1\text{e-}20$ molecule⁻¹cm³s⁻¹ at 298 K. [Calvert et al., 2002] Taking the example of 1,3,5 TMB, at the peak hydrocarbon and ozone mixing ratios observed at any point during the experiment (275 ppbv and 396 ppbv respectively), the maximum (stabilised) Criegee

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concentration in the chamber is calculated to be ca. 2×10^5 molecule cm^{-3} (assuming 40 % of excited criegee biradicals undergo stabilisation, and a lifetime of 1 s for these stabilised criegee species- in practice their lifetime is likely to be an order of magnitude lower than this due to reaction with NO). Thus even if reactions of the stabilised criegee species generated OH with unity quantum yield in the fluorescence chamber, the level of interference would be much lower than the discrepancy in the observed (LIF vs. FTIR) OH levels (8×10^6 molecule cm^{-3}) in the 1,3,5-TMB experiment. Concentrations of the excited criegee intermediate are expected to be orders of magnitude lower.

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