

# **Interactive comment on: “*Pressure dependent calibration of the OH and HO<sub>x</sub> channels of a FAGE HO<sub>x</sub> instrument using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)*”**

**F. A. F. Winiberg et al.**

We would like to thank the reviewer for their constructive review and positive recommendation for publication. We have addressed the points raised in order (highlighted in blue).

Most of the measurements were done using the HIRAC FAGE instrument, which appears to be similar in design to the aircraft FAGE instrument except for the different laser systems. However, it is not clear from the information provided whether the two instruments are indeed identical in their inlet length, inlet size, operating pressure, etc. Although it appears both instruments were calibrated in the chamber for HO<sub>2</sub>, it appears that only the HIRAC instrument was calibrated in the chamber for OH. The authors should provide more details regarding the specifics of each instrument (inlet length, etc.) to show that the results from the HIRAC FAGE instrument are applicable to the aircraft instrument.

The University of Leeds HIRAC FAGE instrument was designed based on the aircraft instrument, and hence they are very similar (electronics, detectors, cell design etc.). To clarify differences, we have added an extra column to Table 1 which addresses the differences and amended the first paragraph of section 2.2 (p. 7972, l. 15), which now reads:

*“...Table 1. The two FAGE systems were very similar in design except for the inlet length and pinhole size, highlighted in Table 1. The aircraft instrument was used as described...”*

We have also tried to emphasise and clarify these points throughout the rest of section 2.2.

The authors make note of the known interference associated with the detection of certain organic peroxy radicals and state that this interference is negligible for these experiments. However, the authors should be more explicit in describing this potential interferences in their experiments, as the HO<sub>2</sub> calibration experiments (both the H<sub>2</sub>O photolysis and HCHO photolysis) do not appear to generate any RO<sub>2</sub> radicals that could interfere with their measurements of HO<sub>2</sub>.

The reviewer is correct in stating that neither of the HO<sub>2</sub> calibration processes create any RO<sub>2</sub> that could interfere with measurements of HO<sub>2</sub> and we have now clarified this point in the text (p. 7973, l. 11):

*“...of a further publication. The potential interferences associated with HO<sub>2</sub> measurements in the presence of certain hydrocarbons due to the presence of β-hydroxyperoxy radicals do not apply to either of the HO<sub>2</sub> calibration methods. In addition, any interference from RO<sub>2</sub> radicals produced during the alternative calibration methods was experimentally demonstrated to be negligible under the conditions of these experiments (Winiberg, 2014).”*

The authors do not address potential interferences with measurements of OH other than that generated by their 200 Hz laser. Recent studies have suggested that there may be significant non-laser generated interferences associated with some FAGE instruments (Mao et al., 2012; Novelli et al., 2014 in the references). It has been suggested that the interference may be due to the decomposition of Creigee intermediates produced from the ozonolysis of alkenes (Mao et al., 2012; Novelli et al., Phys. Chem. Chem. Phys., 16, 19941-19951, 2014). The authors should comment on this potential interference in their OH decay experiments in *iso*-butene, and what these measurements might imply about the sensitivity of their instrument to this interference.

In the absence of either deep UV or NO<sub>2</sub>, concentrations of O<sub>3</sub> were measured and observed to be low (<40 ppbv) in the system with *iso*-butene. As stated in the text, under these conditions we would expect ~98% of the loss of *iso*-butene to be due to reaction with OH. Additionally, the potential for complications from such secondary chemistry and/or interferences was tested by using a number of different hydrocarbons, and in the particular case of interference resulting from O<sub>3</sub> + HC reactions we used cyclohexane and n-pentane which have extremely low or unmeasurable rate of reaction with O<sub>3</sub>.

### Specific comments:

**Page 7980:** Laser generated OH. The authors note that the lower repetition rate laser produced OH from the photolysis of their OH precursor tertbutylhydroperoxide in the dark, and suggest that it is laser generated due to the quadratic increase in this signal with laser power. Did the authors add the internal OH scavenger during this dark period to show that this signal does not decrease, consistent with laser-generated OH?

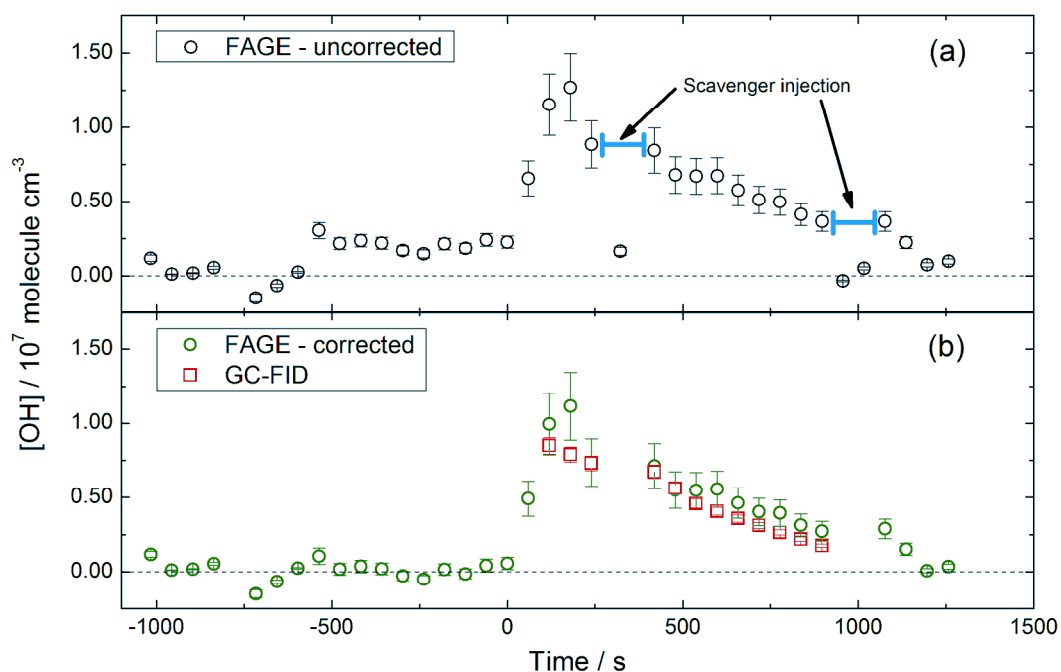
Yes. During some initial tests when the interference was first seen, we decided to fit the internal scavenger system and negligible difference was observed in the OH fluorescence signal before and during the scavenger injection. This comment has now been included in this section.

Was this laser generated OH constant during the experiment?

No. The scavenger data described the decay of the TBHP over time and an empirical fit to this data (linear or exponential) was used to correct the FAGE signal as a function of time. This has now been clarified in the manuscript.

In Figure 6, periods when the OH scavenger was added are shown, but the resulting OH concentration are not shown. It appears that the level of OH measured during the initial dark period was subtracted from the overall signal, and that the measured OH with the scavenger should be similar to this concentration. The authors should show in this Figure the remaining OH concentration during the scavenging period and whether it is consistent with the laser generated OH measured during the dark period.

The OH interference measured in the scavenger injection periods has been added to Figure 6 to more clearly show the decay of the interference over time (see below). The signal was consistent with the interference measurement before the chamber photolysis was initiated and the decay of the *tert*-butylhydroperoxide (TBHP). In a separate experiment we confirmed that the decay of the TBHP (measured using FTIR) was accurately described by the monitored decay in the FAGE interference signal using more frequent injections of the *iso*-butane scavenger. These points will be included in the manuscript to clarify the change in interference signal during and experiment.



**Page 7975:** Water vapor calibration of  $\text{HO}_2$ . Did the authors simply assume that the  $[\text{HO}_2]=[\text{OH}]$  in their system?

Yes. The  $\text{H}_2\text{O}$  photolysis calibration method using a turbulent flow of humidified air is the most widely used technique, and recently Fuchs et al. (2013: see reference in manuscript) were able to show that all H atoms produced reacted with  $\text{O}_2$ , hence  $[\text{OH}] = [\text{HO}_2]$  at the inlet.

How did they calibrate the conversion efficiency of  $\text{HO}_2$  to OH? Did they confirm this through conversion of OH to  $\text{HO}_2$  through the addition of CO to the calibrator to convert the OH produced in the calibrator to  $\text{HO}_2$ ?

In the past we have used CO in the calibrator to show that  $[\text{HO}_2] = [\text{OH}]$  following the photolysis of  $\text{H}_2\text{O}$ , and this was how the conversion efficiency was calculated by (Malkin 2010). However, we felt that inclusion of more detail in this area would detract from the main focus of the manuscript as it was not necessary to know the  $\text{HO}_2$  conversion efficiency to determine the instrument sensitivity.

**Page 7984:**  $\text{HO}_2$  sensitivity vs. pressure. The  $\text{HO}_2$  sensitivity for the HIRAC instrument shows a greater dependence on pressure compared to the OH sensitivity, which the authors attribute to a change in the conversion efficiency of  $\text{HO}_2$  to OH due to differences in the mixing efficiency of NO into the airstream at different pressures.

Did the authors measure the HO<sub>2</sub> to OH conversion efficiency for each pressure (using different inlet diameters and the water vapor calibration technique) to support this?

We did not determine the HO<sub>2</sub> conversion efficiency as a function of pressure, and the discussion point offered in the manuscript was a hypothesis to attempt to explain the difference in pressure dependence of the instrument sensitivity to OH and HO<sub>2</sub>, as the true reason for this deviation is not known. In the future we hope to investigate the conversion efficiency as a function of pressure, along with the conversion efficiency of several RO<sub>2</sub> radicals to OH also.

Malkin, T. L. (2010). Detection of free radicals and other species to investigate atmospheric chemistry in the HIRAC chamber. PhD, University of Leeds.