

Interactive comment on “Pressure dependent calibration of the OH and HO_x channels of a FAGE HO_x instrument using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)” by F. A. F. Winiberg et al.

Anonymous Referee #1

Received and published: 10 September 2014

This paper presents a series of calibrations of a FAGE (Fluorescence Assay by Gas Expansion) instrument for the measurement of OH and HO₂ radicals. The FAGE technique has been used by a number of research groups to measure these radicals both on the ground and on aircraft. Many of these measurements have been greater than predicted by current models, questioning both the accuracy of the measurements as well as the models. In contrast to long path Differential Optical Absorption Spectroscopy (DOAS), measurements of OH using the FAGE technique are not absolute and must be calibrated to determine OH concentrations.

C2579

This study provides additional experimental evidence regarding the accuracy of several methods for calibrating FAGE instruments, including the photolysis of water in a flow tube for calibrating both OH and HO₂, the decay of hydrocarbons for calibrating OH, and the loss of HO₂ due to recombination for calibrating HO₂. In contrast to previous studies, the latter two techniques were done at different ambient pressures inside the HIRAC chamber, providing a test of traditional calibration methods under external pressure conditions similar to that experienced by aircraft FAGE instruments. The authors find that the three calibration methods agree with each other to within the uncertainty of each technique. In addition, the authors find that calibrations at different external pressures (leading to different internal pressures in the FAGE instrument) are consistent with calibrations done using different inlet sizes at atmospheric pressure to vary the internal pressure of the FAGE instrument. The results give additional confidence in the accuracy of field measurements of OH and HO₂ radicals and in particular aircraft FAGE measurements and is suitable for publication in AMT.

General comments:

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 HO₂, 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 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 HO₂ calibration experiments (both the H₂O

C2580

photolysis and HCHO photolysis) do not appear to generate any RO₂ radicals that could interfere with their measurements of HO₂.

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.

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? Was this laser generated OH constant during the experiment? 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.

Page 7975: Water vapor calibration of HO₂. Did the authors simply assume that the [HO₂]=[OH] in their system? How did they calibrate the conversion efficiency of HO₂ to OH? Did they confirm this through conversion of OH to HO₂ through the addition of

C2581

CO to the calibrator to convert the OH produced in the calibrator to HO₂?

Page 7984: HO₂ sensitivity vs. pressure. The HO₂ 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 HO₂ to OH due to differences in the mixing efficiency of NO into the airstream at different pressures. Did the authors measure the HO₂ to OH conversion efficiency for each pressure (using different inlet diameters and the water vapor calibration technique) to support this?

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 7963, 2014.

C2582