

Interactive comment on “Reporting the sensitivity of Laser Induced Fluorescence instruments used for HO₂ detection to an interference from RO₂ radicals and introducing a novel approach that enables HO₂ and certain RO₂ types to be selectively measured” by L. K. Whalley et al.

Anonymous Referee #2

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This paper presents measurements of interferences in the detection of HO₂ radicals by various RO₂ radicals in several FAGE instruments used by this group in the past. Recent measurements have shown that detection of HO₂ radicals by chemical conversion to OH through reaction with NO can be sensitive to the detection of select RO₂ radicals. The degree of interference likely depends on the characteristics of the instrument (flow velocity, inlet geometry), thus each individual instrument must be calibrated

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for this interference in order to accurately interpret past and future measurements using this technique. Similar to other FAGE instruments, these authors find that several of their instrument configurations are sensitive to the detection of alkene and aromatic derived peroxy radicals, and provide some discussion on the impact of this interference on their previous measurements. The paper is well written and appropriate for publication in AMT after the authors have addressed the following comments:

1) The authors present two methods for determining the conversion efficiency of RO₂ into OH – their OH and HO₂ calibration system using a turbulent flow reactor that generates a steady state concentration of radicals using a mercury pen-ray lamp, and a flow tube system that incorporates a time-dependent source of radicals through laser-flash photolysis techniques. Unfortunately it is not clear why two the two different techniques were used, as it appears that each technique was used to calibrate different FAGE instruments. The authors should clarify why the time-dependent source of radicals was used, why the interference for the different field FAGE instruments were not cross calibrated with this technique, and why a fourth FAGE instrument with a different geometry compared to the field instruments was used, which was also not cross-calibrated with the steady-state field reactor.

2) For the time-dependent radical source experiments, the authors compare the decay of converted OH radicals in the FAGE instrument from different RO₂ radicals generated in the flow tube, using the coefficient of the exponential as a measure of the converted RO₂ radicals, comparing it to the exponential from the experiments with methanol, which produce only HO₂. The cause of the decay of radicals in the flow tube is not discussed, but self-reactions of the peroxy radicals likely contribute. It is not clear from the discussion why the authors used this approach, and the data shown in Figure 3 is somewhat confusing. It appears to show that the conversion efficiency of RO₂ to OH is high for isoprene and low for the alkanes. However, without information regarding the relative radical concentrations used in these experiments it is difficult to interpret the different figures. Were the initial OH concentrations (signals) and decay rates in

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the absence of NO the similar for all experiments, suggesting that the RO₂ concentrations were similar? Are the decay rates of each consistent with the estimated RO₂ concentration and MCM rate constants? It appears that the OH decay in the top panel the Figure is for a lower isoprene concentration than the converted RO₂ signal for isoprene in the bottom panel. Does the FAGE OH signal in the bottom panel includes signal from both unreacted OH and converted RO₂? If so, why is the FAGE OH signal for the alkanes lower than the initial OH signal? The paper would benefit from additional information and clarification of how the data in these experiments were used to extract the RO₂->OH conversion efficiencies. Did the authors model the production and loss of the different RO₂ radicals in the flow tube?

3) In Figure 6, the authors demonstrate that reducing the concentration of NO can reduce the RO₂-> OH conversion efficiency. However, it is not clear which FAGE axis design and reaction time corresponds to the measurements/model. Is this the FAGE cell with 10 ms of reaction time used in the time dependent radical source experiments, or the field FAGE cell with 1 ms of reaction time? Given that there are mixing issues associated with injection of NO for each FAGE cell, the authors should demonstrate that the field FAGE cells are able to minimize (and maximize as a measure of alkene and aromatic RO₂) the RO₂ interference.

4) The authors attempt to summarize the impact of the interference on their previous measurements in section 4.3. It would be helpful to summarize this information in a Table that includes the campaign, a reference to the original analysis, the original model/measurement agreement for HO₂, which FAGE cell was used, the average alkene/alkane RO₂ conversion efficiency from this paper, and the impact of the interference on the previous conclusions.

5) In Figure 7, the authors illustrate the ability of one FAGE axis (cell a) to selectively detect HO₂ (at low added NO) and alkene/aromatic/long chain aliphatic derived RO₂ (at high added NO) and compare it with the measured total RO₂ using FAGE cell (c). The authors should clarify whether the concentrations shown in this Figure are derived

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from Equations 7 and 8, or whether these are the results of the different measurements modes, where the HO₂ concentrations are the measurements from cell (a) at low added NO, the alkene/aromatic/long chain aliphatic RO₂ concentrations are the measurements from cell (a) at high added NO (with the measured HO₂ concentrations subtracted), and the aliphatic RO₂ are the measurements from cell (c) with the high NO measurements from cell (a) subtracted. In either case, it would be useful to include the measured total RO₂, HO₂^{*}, and HO₂ to help clarify what is actually measured and what is derived from the individual measurements.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 6249, 2013.

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