

Interactive comment on “Investigation of potential interferences in the detection of atmospheric RO_x radicals by laser-induced fluorescence under dark conditions” by H. Fuchs et al.

Anonymous Referee #2

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This paper presents measurements of several instrument artifacts that could potentially interfere with the measurement of OH radicals by the LIF-FAGE technique. Several recent LIF-FAGE instruments have reported instrument artifacts that could explain the higher-than-expected measurements of OH reported in low NO_x/ high biogenic environments (Roher et al., 2014). The authors conduct several experiments both in the laboratory and in the SAPHIR chamber to identify potential artifacts. They find that under typical ambient concentrations of ozone and several biogenics their FAGE instrument does not detect any instrumental artifacts. However, when high concentrations of ozone are reacted with high concentrations α -pinene, limonene, or isoprene, a measurable OH artifact detected. In contrast to previous studies, the authors do not believe

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that the artifact is due to the decomposition of Creigee intermediates in their detection cell, as addition of SO₂ as a Creigee scavenger does not appear to remove the interference. The observed interference is strongly correlated with the rate of ozonolysis turnover, and their results suggest that at atmospherically relevant turnover rates the interference would be negligible.

In addition, an OH artifact is detected under dark conditions when high concentrations of NO₃ are introduced, with approximately $1 \times 10^5 \text{ cm}^{-3}$ OH produced from 10 pptv of NO₃. The authors speculate that the OH artifact in these experiments might be due to heterogeneous reactions of NO₃ on the interior walls of their detection cell or decomposition of molecular clusters in the low pressure expansion.

The paper is generally well written and the experiments described provide new information on potential artifacts with LIF-FAGE measurements of OH and peroxy radicals. In their revision the authors should address the following questions:

1) In the ozonolysis experiments, the authors add enough propane to remove OH produced in the flow tube and claim that since the OH from the ozone interference is not removed then any internally generated OH is not scavenged. However, if the mechanism of the ozone interference is different than that for other artifacts, the reaction time with propane of the OH produced from the ozone interference may be different than that for other artifacts. Thus it is possible that the added propane may have removed internally generated OH artifacts that were not produced by the ozone interference. However, if the ozone interference behaves similarly to the ozonolysis interference, then it is possible that the mechanisms are similar. Does the ozone interference increase with increasing inlet length, similar to the observed ozonolysis interference? Does it increase with increasing residence time in the cell?

2) One way to insure that no internally generated OH is titrated by the added propane is to produce OH internally and determine whether it is scavenged. Did the authors perform experiments where they produce OH internally near the inlet and with the

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longest reaction time (similar to that described in Mao et al., 2012) to insure that the added propane is not scavenging any OH produced inside their detection cell?

3) In the flow tube ozonolysis experiments described in Table 1, are the OH concentrations produced in the absence of propane consistent with the expected OH yield given the concentrations of ozone and the alkene? This would provide some additional evidence that the measured OH under these conditions is not influenced by instrument artifacts.

4) The authors suggest that the observation that the artifact from the ozonolysis of α -pinene does not change in the presence of SO₂ implies that sCIs from α -pinene ozonolysis are not the source of the artifact based on the observed rate of SO₂ oxidation by sCIs by Sipilä et al. (2014). However, the results of Sipilä et al. (2014) reflect the average reactivity of all sCIs produced in the ozonolysis of α -pinene. Thus it is possible that the artifact is due to a particular sCI that does not react efficiently with SO₂. This should be clarified in the manuscript, as it does not necessarily rule out sCIs as the cause of the interference. Did the authors try adding a different sCI scavenger, such as an organic acid that may react differently with the sCIs than SO₂ (Sipilä et al., 2014)?

5) The authors suggest that the NO₃ interference could explain some of the discrepancies between HO₂ measurements in the dark during the HOxComp campaign. Could this interference also explain the unknown interference with OH measurements in the dark found for one of the LIF instruments as described in Schlosser et al. (2009)?

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