Atmos. Meas. Tech. Discuss., 8, C4541–C4545, 2015
www.atmos-meas-tech-discuss.net/8/C4541/2015/

Atmospheric Measurement Techniques Discussions

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 #1

Received and published: 30 December 2015

General comments:

This manuscript describes potential interferences in the detection of atmospheric ROx radicals under dark conditions by the laser-induced fluorescence instruments employed by the Forschungszentrum Jülich. The authors investigated potential interferences related to the nitrate radical, ozonolysis of alkenes, and the photolysis of acetone. The Jülich LIF instruments do produce OH internally in the presence of NO3, but the authors suggest this interference should be negligible for ground based measurements. Under most atmospheric conditions, the authors report negligible interferences from the ozonolysis of alkenes, only observing significant internal OH production with ex-

ceptionally high reactant concentrations. Interestingly, the observed internal OH signal does not change in the presence of SO2 for the case of α-pinene ozonolysis, suggesting that decomposition of Stabilized Criegee intermediates is unlikely the reason for internal OH production in these instruments. This is in contrast to the reports of at least one other LIF instrument.

The experiments were performed with two instrument configurations, one with a short inlet and an aircraft instrument with a longer inlet. The major concern I have is the experimental parameters that were employed with the two different configurations. If the critical orifice and therefore the sampling flow rate is the same for the short and long inlet (0.4 mm, 1 slm, Pg 12480 Line 19), why is a different laser repetition rate used for the two configurations? Is this the normal operational configuration that the long inlet and the short inlet have the same critical orifice diameter? If not, I think this is a major point that needs to be addressed because the tests were not carried out under normal operational conditions for one (or both?) configurations.

The manuscript is well written, and is a valuable addition to the investigation of interferences in the LIF detection of ROx radicals. The topic is timely and a good fit for the journal. I would recommend reconsideration of the publication after addressing the major point above and additional comments below.

Additional comments:

1. The short inlet and long inlet configurations differ not only in inlet length but also in nozzle design. How much influence does the nozzle itself have? Have tests been done with placing the skimmer nozzle on the long inlet and the drilled nozzle onto the short inlet?

2. Calculated/estimated residence times within the inlets are given on Pg. 12481. Would it be possible to measure the residence times instead; as this would eliminate the need to make assumptions about the flow patterns.

3. Can you quantify the interference from acetone photolysis for the long inlet/lower repetition rate configuration?

4. What is the ozone interference for the instrument with the short inlet and higher repetition rate? Is this ozone interference always subtracted from the measurements obtained with the FZJ LIF instruments?

5. Ozonolysis experiments were done with the long inlet. I think it would be valuable to see the results for the short inlet as well, and would be also beneficial to have several other inlet lengths (and therefore residence times) in between those. From Novelli et al. (PCCP 2014), at least for the MPIC LIF instrument, it seems as though there is a peak residence time for "optimal interference" and it would be interesting to see if the FZJ instrument shows something similar.

6. Since the residence times are just estimates and it's unclear where/what process is generating the internal OH signal, how can you be sure that propane is not scavenging internal OH? Pg. 12489 Lines 5-7 suggest that since the ozone interference signal is constant that no internal scavenging is taking place. But if the internal OH resulting from ozonolysis is being generated directly after the nozzle in the gas expansion, then depending on the cell configuration, the OH interference generated by ozone photolysis is taking place at a later time.

7. The magnitude of the interference signal for the ozonolysis experiments is larger for the long inlet configuration (Pg. 12490 Line 19-20). Any speculation on why this might be?

8. Table 1 lists laser power as around 13 mW. Was this the case for both inlet lengths/repetition rates? Is that the normal operational power?

9. Figure 7 mentions "Subtraction of an offset in OH by LIF." What is this offset? Is it the unexplained/interference OH?

Technical comments:

Pg. 12476 Line 12: "overflown" is incorrect usage, should be over flowed (this error of flown instead of flowed occurs quite often)

Pg. 12478 Line 16: "allows to destroy" change to "destroys"

Pg. 12484 Line 1: "was flown" should be "was flowed"

Pg. 12484 Line 6-7: "propane, propene" replace with "propane and propene"

Pg. 12484 Line 8: remove comma after 2,3-dimethyl-2-butene

Pg. 12485 Line 1: "was flown" should be "was flowed"

Pg. 12485 Line 2: add "an" before NO3/N2O5 source

Pg. 12485 Line 14: lower case instability

Pg. 12485 Lines 18-20: Sentence starting with "These experiments…" is awkward. Perhaps change to "The experiments allowed the comparison of OH measurements by the LIF instrument…..."

Pg. 12486 Line 11: comma after experiment

Pg. 12486 Line 13: Fuchs et al. (2009) and (instead of semicolon) Wagner et al. (2011).

Pg. 12489 Line 24: remove comma after both

Pg. 12490 Line 6: remove comma after conducted

Pg. 12491 Line 3: add comma after Also

Pg. 12491 Line 13: "reached then" change to "then reached"

Pg. 12493 Line 10: remove s on productions

Pg. 12494 Line 9: replace "and" after α-pinene with comma

Pg. 12494 Line 26: remove comma after conditions

Pg. 12495 Line 5: remove “that it”

Pg. 12495 Line 10-11: rewrite as “The maximum propene concentration used here, and therefore also the production rate of sCIs in the flow tube, was 7 times smaller.”

Pg. 12497 Line 3: remove commas after conducted and test

Pg. 12497 Line 9: remove “respectively”

Pg. 12502 Line 15: typo “oder”

Pg. 12503 Line 6: change “photolytical” to “photolytic”

Figure 1 caption, last sentence: remove comma after placed. Remove s on lasers

Figure 2 caption, second sentence: “flown” should be “flowed”

Figure 3 caption, second sentence: “overflown” should be “over flowed”

Figure 6: change color scheme to be consistent through all 4 subplots. i.e. “short inlet” should be red in each case

Figure 11: are these measurements with the short or long inlet?

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 12475, 2015.