

Atmos. Meas. Tech. Discuss., referee comment RC1
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Comment on amt-2021-102

Anonymous Referee #1

Referee comment on "Development of a laser-photofragmentation laser-induced fluorescence instrument for the detection of nitrous acid and hydroxyl radicals in the atmosphere" by Brandon Bottorff et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-102-RC1>, 2021

The authors aim for describing a new instrument for the detection of HONO by laser-photofragmentation of HONO and subsequent detection of OH by LIF. Although the topic of the paper would have been in the scope of this journal, the way the authors structure the paper is not appropriate. The authors give an adequate clear description of the instrument and its calibration.

However, the results and discussion part is not fitting the scope of the journal. The authors mainly describe measurements and try to give a chemical explanation of the observed concentrations. This is clearly out of the scope of this journal and should be significantly shortened. Unfortunately, the authors give only little results and discussion of the performance of the instrument. Even the discussion of interferences is kept on a level of estimates from literature and the only experimental result is only mentioned to be discussed in future publications. More detailed experimental investigations in the laboratory could have been done.

A comparison of the measured HONO/OH ratio with calculations could have been valuable, if this is used to test the validity of the instrument. However, this is likely not possible, because concentrations are not only determined by the photo-stationary state of gas-phase reactions and the additional measurements may be incomplete or not of high-enough quality. Another option would have been to include a detailed comparison with the CIMS instrument, but the author decided not to do so, but to shift this to another publication.

Overall, the authors mention topics that could have been discussed to show and discuss the performance of the instruments even without further experiments, which would have been even better. Because of the lack of content, I recommend rejecting the paper. It might become suitable for the journal, if there is a broader discussion of results.

Detailed comments to the part of the experimental section:

L13: Full calibration of the sensitivity requires also the calibration of the OH detection sensitivity.

L16: Does the LOD refer to HONO and OH?

L39: The explanation of HONO accumulating during nighttime is a bit misleading, because gas-phase reaction alone would not explain the increase of HONO during the night, but only shift the photo-stationary state to HONO at dawn.

L166: Here or somewhere else the authors should mention the duration of each step in the measurement cycle.

L211/L213: There is inconsistency in the naming of the quantum yield.

L233/234: The term "effective sensitivity" is rather confusing in this context. The sensitivity of the instrument does not depend on laser power due to the normalization of the fluorescence signal to the laser power. The authors likely mean a better limit of detection that can be achieved at higher laser power, because the total fluorescence counts increase and is therefore more likely larger than the noise. Please clarify.

L233/234: The authors argue that photolytic interferences become smaller in the single-pass configuration compared to the multi-pass configuration. This would allow to operate the system at higher laser power. This is rather confusing because at higher laser power photolytic interferences will again gain in importance. Please clarify.

L242: What do the authors mean with "once a stable concentration OH and HO₂ is produced"? What does need to stabilize?

L249: How was the loss of 5% determined?

L250: It would be beneficial for the reader to know the wall loss rates that are assumed and to specify the fractional loss to specific loss processes.

L252: The text sounds as if there is a significant fraction of OH left, but Fig S4 suggests that this is negligible.

L252: Can the authors exclude that reactions of NO from the calibration source leads to any back-reaction of OH to HONO after the 355nm laser pulse has been applied in the measurement cell?

Figure 4/5: Are really counts shown or normalized count rates? Why are numbers in Fig. 4 so much smaller compared to numbers in Fig. 5, if they are also derived from calibration measurements?

L267: It is not very clear for the reader, which correction is applied to S_OH. Is this needed because different losses apply, if NO is added or not? Number of corrections may help to better understand what is done.

L271: The authors mention several possible problems with impurities of the NO added in the calibration procedure. This discussion should be extended by a quantitative estimate, if these reactions could play a role for the conditions described in this work.

L282: It would help to give a quantitative estimate about the impact of a typical additional OH concentration during midday on the limit of detection of HONO.

L283: Typical accuracies for the determination of OH concentration in a calibration source like used in this work are within the range of 10 to 20% and would significantly contribute to the overall uncertainty of the HONO calibration. Please clarify.