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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Interferences in photolytic NO_2 measurements: explanation for an apparent missing oxidant?" *by* C. Reed et al.

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We thank the reviewer for taking the time to provide us with a thorough review for the paper. We have made the changes that they have suggested as we believe that this has significantly improved the paper.

We address their comments in turn now.

"It does not seem they've considered the possible interferences posed by methyl pernitrate (CH3O2NO2), as discussed by Browne et al., ACP, 11, 4209–4219, doi:10.5194/acp-11-4209-2011, 2011. It would be worth including in the discussion as it touches on measurements in the UTLS."

The authors have indeed considered methyl pernitrate as a source of interference men-

tioning it several times; in the abstract pp 28700 line 18, pp 28722 line 19, and in figure 8, including it in our model. However we have now made it clear that methyl pernitrate is the dominant source of error in the upper troposphere (from our model) citing the reviewers suggested paper (Browne et al., 2013) and (Nault et al., 2015).

"The authors may wish to call attention to another cause of spurious deviations from expected NO2:NO ratios based on photolytic NO2 measurements at low ambient mixing ratios, described in Appendix A of Yang et al., JGR, 109, D02312, doi:10.1029/2003JD003983, 2004."

We would like to thank the reviewer for drawing to our attention what is a very comprehensive and detailed description of the inherent bias in statistical techniques and averaging used to calculate NO2 from NOx measurements. We have added a discussion and the appropriate citation of Yang et al. findings.

"One difficulty of this kind of paper comes in generalizing from their instrument to all other instruments. A note is made in the abstract that “Although this interference is likely instrument specific. . .” but the at times the text seems to imply they believe this may be more a general problem. The paper makes a strong case that the commercial “Blue Light Converters” (BLCs) they tested do exhibit this problem generally, but also cite a report that used a very different setup with a mercury arc lamp where PAN conversion was tested directly and found to be negligible. The commercial BLCs used in the present report have UV-irradiated, sample-wetted surface materials (stainless steel, PTFE Teflon, LED chips etc.) that are not present in all other designs. Perhaps reconsidering the degree to which they generalize conclusions from the BLCs to other designs – or better, if they could, recommending materials that do not lead to their observed interferences? - would be warranted."

Indeed, it is the contacting of sample gas with the UV emitting elements which are necessarily hot which is the source of bias – which is absent in different set-ups such as with a mercury arc lamp; The reviewer is likely referring to the work of Ryerson

ACPD
15, C13373–C13377, 2016

et al., (2000) who found negligible PAN interference – surface mediated or otherwise. We have, in our conclusions, made it clear that any system that heats a sample gas above ambient has the potential for interference and that the BLC method of contacting the sample with sometimes very hot LEDs is not optimal for accurate NO2 determination. We recommend separating the UV emitter from the sample gas by e.g. quartz glass which has excellent UV transmission. In addition, but a separate subject, quartz being non-porous and very inert minimises any zero artifact or memory effect. The paper could make a clearer distinction between gas-phase thermal decomposition of PAN, which is a straightforward calculation, and the possibility of surface-mediated decomposition of PAN on irradiated and heated surfaces. It was beyond our capabilities to, with any certainty, discriminate between gas phase and surface mediated decomposition (again, as with Ryerson et al., (2000)) in such a complex system. We have performed various thermal decomposition experiments with NOy species and found the material to be important. Below in Fig. 1 is the measured NOx from the decomposition of n-Propyl Nitrate (chosen because of exhibiting little decomposition with the BLC) over pure quartz and over quartz/315 stainless steel.

Figure 1 shows purely gas phase model of n-Propyl Nitrate decomposition with 1 s residence time with data from IUPAC (Atkinson et al., 2006) is shown in black, the decomposition profile of the same passed through a completely quartz/quartz packed furnace in red, and in green passed through a 316 stainless steel/quartz packed furnace.

Clearly the pure quartz performs much better than steel, even at low temperatures, at replicating the model, which is unsurprising given the transition metals present in stainless steel, such as molybdenum – a NO2 reduction catalyst in its own right. Obviously the BLC has anodized aluminium; Teflon; conformal coating; epoxy resin; steel; and rubber contacting the sample gas at moderate but not excessive temperatures possibility for surface enhanced/heterogeneous decomposition exists. However we have no quantitative measure of this.

ACPD
15, C13373–C13377, 2016

We have highlighted the possibility and distinction of heterogeneous processes in the discussion, suggesting quartz to be an ideal alternative material for a converter due to being inert and UV transparent in light of Ryersons' (Ryerson et al., 2000) previous findings.

References

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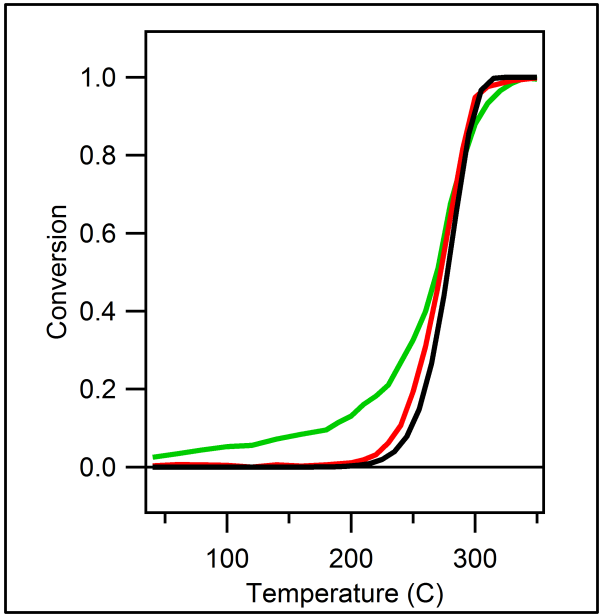

Fig. 1. n-Propyl nitrate decomposition over quartz and stainless steel

ACPD
15, C13373–C13377, 2016

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