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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.

Anonymous Referee #2

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This is a clearly written paper that should help to resolve problems with measurements based on photolysis of NO2 followed by chemiluminescence detection of NO. They give compelling reasons that many of the exciting "compounds X" invoked are likely unneeded, due to a more mundane measurement interference from PAN.

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 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.

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.

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.

This will make a solid contribution to ACP once these relatively minor issues are addressed.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 28699, 2015.