

Atmos. Meas. Tech. Discuss., referee comment RC2
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Comment on amt-2021-180

Anonymous Referee #3

Referee comment on "Modification of a conventional photolytic converter for improving aircraft measurements of NO₂ via chemiluminescence" by Clara M. Nussbaumer et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-180-RC2>, 2021

The authors describe an implementation of a photolytic NO₂ converter demonstrating it's' use in airborne atmospheric research – specifically high altitude aircraft measurements. The selective photolysis of NO₂ using a narrow band UV source illuminating a quartz cell, followed by detection of the resulting NO by chemiluminescence has been the reference method of NO_x determination since the early 2000s'.

With some comments addressed the manuscript can make a valuable contribution to AMT.

General comments:

The authors don't give a clear rational for modifying of the Droplet Measurement Technologies (also Air Quality Design, and now Teledyne API) Blue Light Converter in the way they have, especially given the sub-optimal results.

Why reuse the low-powered 1 W, 395 nm, UV Hex, Norlux Corp. LEDs when much more powerful units are available – and in fact are used in more recent BLCs (see: <https://doi.org/10.5194/amt-9-2483-2016>)?

What is the rational for moulding the PTFE around the quartz envelope? Were no alternatives tried? Similar aircraft implementations from NOAA, NCAR and FAAM, plus the paper cited by Andersen et al., 2021 use quartz cells wrapped in baking foil! Vapour deposition of optical silver has also been used in the past with no benefit over simply wrapping.

I realise in advance the answer to the two previous questions may be due to certification

hurdles of HALO/DLR.

The authors should note that their PLC/BLC implementation has remarkably similar characteristics to a once commercially available unit also marketed by Droplet Measurement Technologies – a glass envelope, shrouded in PTFE, with arrays of Norlux UV-LEDs at either end. In this case the volume is $\sim 115 \text{ cm}^3$ which is the main difference. It is well described in the paper by Pollack et al., 2010 which the authors cite. These NO₂ converters were previously operated by NCAR and FAAM on their aircraft, though are long since retired.

There is a marked drop in photolysis frequency between the two BLC modifications (0.66 to 0.46) using presumably the same LEDs. The authors should discuss why this is the case; is it the design, or aging of the LEDs, change in sample gas temperature etc.

There is no description of the aircraft inlet from which the NO_x instrument samples. Is that heated? What is the residence time to the instrument? What is the sample line/cabin temperature? When discussing the uncertainty of airborne measurements these must be taken into account.

There is no schematic of the instrument given so I must assume it is identical to F2 given in Tadic et al., 2020. Several elements of the design shown there may skew measurements, especially during your discussion of the effects of humidity.

Firstly, the sample flows through mass flow controllers in the high pressure side of the inlet system which a) increases hold-up/lag, but also provides plenty of stainless steel surfaces to form layers of water on. Secondly, the NO and NO_x channels appear to have different volumes due to there only being an NO₂ converter on the NO_x channel and no dead cell on the NO channel. Necessarily, there are different surface areas between the two, and different volumes, thus data must be offset between the two channels to compensate for the different residence times which themselves must either be very carefully measured or modelled. I doubt for instance that the true residence time if the BLC is 0.34 seconds – this is more likely 1 e-folding time. Lastly, and most crucially, the flow of humidified ozone is switched between reaction and pre-chamber of the CLD, with the sample (of varying humidity) constantly passing through the pre-chamber. This results in wildly fluctuating humidity within the pre-chamber. Many airborne CLDs follow the scheme in Pollack et al. 2010 whereby the humidified ozone constantly passes through the pre-chamber and the sample is switched – this also acts to decrease the response time of the instrument by removing dead volume.

Ultimately, I don't think flaws in the instrument design can account for the humidity effects described, though they should be considered.

The whole discussion on possible mechanisms for NO/H₂O selective/competitive sorption is highly speculative and hard to follow at times.

A typical test flight when commissioning a new NO_x instrument is to fly whilst adding an amount of NO well above ambient to the inlet, performing profiles, orbits, in-cloud, boundary layer, and free troposphere runs – a system which is performing well will show no deviation throughout the entire flight envelope.

Specific comments:

Line 86: this was also the conclusion of Reed et al., 2016 which is cited.

Line 117: 'commercially available' – all four example of the CLD 790 SR were built for DLR on special order, no?

Line 123: State the reason why the photolysis cell is operated at 110 mb i.e. this is a pressure height of ~50kft which is the service ceiling of HALO/G550.

Line 124: The stated wavelength is 398 nm of the UV LEDs – the design wavelength is 395 nm – is this a typo or was it measured (and not shown/described)? If the latter then a lot of energy is being wasted outside of the quantum yield of NO₂ which drops rapidly at ~400 nm.

Line 132: please state the j value along with the conversion efficiency i.e. 0.656 s⁻¹

Line 138: please state the j value along with the conversion efficiency i.e. 0.457 s⁻¹

Line 138: presumably the gas flow doesn't contact the LEDs either in the design depicted in F1b? This would in-turn lead to much less sample heating and have a large impact on any thermal artefacts.

Line 178: limits of detection are only useful when an averaging time is stated, please add this, how many standard deviations are included in the determination of LOD and uncertainty? e.g. 5 pptv averaged over 10 seconds, 3 sigma uncertainty of 6% etc.

Line 146: What is the residence time of the pre-chamber; same as the reaction chamber? What is the efficiency? What is the material?

Line 282: `...monitoring system for pressure...' in an airborne system the pressure must always be known and/or controlled otherwise the conversion efficiency of NO₂ to NO is unknowable, regardless of potential artefacts or not!

Line 370: I'm not sure it is true that there are no trends in the NO channel signal – I think the scale may be helping here – perhaps fit the trends to remove any doubt or adjust the scale.

Line 411 -414: the logic in this statement is flawed – you can only measure NO with a CLD, therefore you only saw NO in your experiment. You could do the same experiment with the BLC connected to a direct NO₂ measurement, or a PAN-GC or a CIMS for that matter and would likely see many compounds desorb.

Sect 2.5: please define all the acronyms for the NO_y species (MPN,PAN...) at their first use.