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Atmospheric Measurement Techniques Discussions

Interactive comment on "Folded Tubular Photometer for atmospheric measurements of NO_2 and NO" *by* John W. Birks et al.

Anonymous Referee #1

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The manuscript describes a miniaturised near-UV photometer for quantifying atmospheric NO2, and with conversion by addition of O3, NO by difference. A full description of this commercially available instrument is certainly within the scope of AMT, the level of detail is generally good, as is the presentation quality. I recommend it for publication in AMT after the issues below are addressed.

Major comments:

1) The instrument detects NO2 by single wavelength absorption at 405 nm using an LED light source in a flow cell. The 405 nm region is attractive for NO2 as there are very few other species absorbing strongly in this region. However, this is also the region where the NO2 quantum yield begins to fall to zero from 400 nm upwards. With the relatively broad output of the LED light source the authors present in figure 5 it could

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be expected that an LED of sufficiently high output to be reliably detected over the 2.1m path-length, and after passing various mirrors, plus the authors' estimated 90% loss, might have sufficient photolysis power to dissociate a portion of the NO2 intended for analysis. The authors should add the NO2 quantum yield to figure 5 and discuss this uncertainty, or else justify why NO2 photolysis is irrelevant/insignificant. Adding the LED wattage or j value would also help, as would contrasting with current NO2 photolysis systems which use LEDs from 385-395 nm with a similar Gaussian output e.g. Buhr 2007; Pollack et al., 2011; Reed et al., 2016.

2) The unexplained effect of cell pressure on retrieved analyte concentration warrants further investigation. As the effect is different between systems it suggests difference in construction or materials used. Varying water vapour equilibrium concentration should be the same between both prototype instruments assuming variables such as cell temperature and coating hygroscopicity are controlled for. Was the system tested with sample drying? Different leakage rates between systems or changes in cell length under vacuum perhaps are more likely. Never the less some more insight on the phenomena is important.

Minor comments:

1) A low pressure mercury lamp is used for generating ozone; this is presumably by illuminating ambient air though this detail is absent from the text and is assumed by the absence of an O2 bottle.

2) How is the conversion efficiency of NO to NOÂň22 verified, and is it stable? Low pressure mercury lamps age and reduce in output, chemiluminescence instruments tend to use corona discharge devices for ozone generation due to their stability and high output. Furthermore mercury lamps must be thermos stated to be stable, is this one? Would this negate the advantage of not needing to calibrate the NO2 measurement?

Technical corrections:

P5 L12 – “FTP” – You haven’t defined this acronym before using it and do not use it again.

P6 L34 – “In other work, we measured black carbon using an LED with maximum emission near 880 nm.” Either show the results, include a reference to that paper, or remove this line as it is left hanging.

P7 L19 - “Voltage Sensitive orifice” The following paragraph describes a pressure controller common to numerous optical absorption systems. Is the name change necessary?

P8 L18 – “. . .nearly plug-flow. . .” I’m not sure what nearly plug flow is however looking at Figure 1 suggests that the sample flow is expanded out and made to take a sharp turn at each fold so I find it difficult to believe there is laminar airflow within the system. Remove the reference to plug flow.

P8 L29 – “Scrubber” – provide references or details of this combination of materials being an effective scrubber as this effects the zero bias of the instrument.

P9 L19 – “atm” use bar/mbar consistently as an alternative.

P15 L29 – “. . .true NO2. . .” I believe is how the Teledyne T500U and T200U/P instruments are marketed too. Better delete this line as it doesn’t add anything.

P16 L9 – insert a space at “. . .O3resulting. . .”

References:

Buhr, M.: Solid-State Light Source Photolytic Nitrogen Dioxide Converter, US 7238328 B2, United States, USTPO, available, 3 July 2007.

Pollack, I. B., Lerner, B. M., and Ryerson, T. B.: Evaluation of ultraviolet light-emitting diodes for detection of atmospheric NO2 by photolysis – chemiluminescence, J. Atmos. Chem., 65, 111–125, doi:10.1007/s10874-011-9184-3, 2011.

Reed, C., Evans, M. J., Di Carlo, P., Lee, J. D., and Carpenter, L. J.: Interferences in photolytic NO2 measurements: explanation for an apparent missing oxidant?, Atmos. Chem. Phys., 16, 4707– 4724, doi:10.5194/acp-16-4707-2016, 2016.

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