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Atmospheric Measurement Techniques Discussions

Interactive comment on "Development of a new Long Path Absorption Photometer (LOPAP) instrument for the sensitive detection of NO_2 in the atmosphere" *by* G. Villena et al.

Anonymous Referee #1

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This is a well thought out manuscript and it should be published after attention to the comments below.

The authors have demonstrated the capability of new LOPAP instrument for NO2 detection. This detector was based on the LOPAP HONO instrument described in previous with modifications to capture and convert NO2 in gas phase to HONO in the stripping solution. Ambient HONO is stripped and discarded prior to NO2 detection. The authors report detection limits of 2ppt/3min. We note that many locations where NO2 is approaching 2ppt are ones that typically have 200-500 ppt of PAN. In these locations the interference from PAN of order 0.5% will be limiting.

The paper suggests the reasons that LIF or CRDS instruments are not widely used has to do with the difficulty of implementation. I disagreeâĂŤthe methods are simple but have had difficulty penetrating the entrenched market for chemiluminescence. I suggest the authors remove their speculation on the subject.

Production and loss of NO2 in inlets has plagued many measurements. The accuracy of the calibration should be referenced to standards at the inletâĂŤmost existing methods are more accurate than typically quoted if a known quantity is inserted into the instrument at the point of detection. Conservative estimates of accuracy include losses/gains in transfer from the atmosphere. I recommend the authors remove their suggestion that NO2 reference standards are unstableâĂŤthat is easy to check, for example by absorption spectroscopy.

I would like to see figure 7 and 10 for the range 0-5 ppb. The large range shown is not particularly demanding of an instrument. Alternatively, the figures can be deleted.

The authors should discuss the possibility of other interferences more comprehensivelyâĂŤin particular PAN and its analogs might decompose to yield NO2 and complex nitrates such as derived from isoprene or other biogenic VOC might hydrolyze in their stripping solution to produce NO2.

In sections 2.2 and 2.3, it is mentioned that the reference intensity of the light source is collected at a wavelength well separated from the main absorption peak to account for variation in light intensity. It will thus be informative to also mention the general calibration interval as well as solution change interval since change of absorption profile will lead to the change in calibration parameter. Also, at the beginning of section 2.2, it is mentioned that NEDA has the tendency of deposition onto the inner wall of the liquid core waveguide. In what timescale does this happen under current recipe of dye solution? Also, does such deposition change the overall solution spectrum in any significant manner?

For calibration of the instrument, the author suggests a simplified 2-point calibration

procedure. However, the corresponding infrastructure is not shown in the instrument schematics.

In section 3.1.2, stripping coil configurations are discussed and condensed reaction rate constant calculated. All of the above calculations are assuming the existence of a stable surface solution layer completely covering the interior wall of the stripping coil. However the material for the stripping coil is not mentioned. This could raise speculation concerning the surface affinity to the stripping solution which appears to be water based. Also, has the residence time of the solution in stripping coils been measured and how does compare to the residence time at the LCW?

For the reported accuracy of 10% which is much larger than 0.5% precision and 1% nitrate standard concentration uncertainty, what is the main contributor to the error? Is it due to the long-term drift of the light source or change in dye condition?

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 1751, 2011.