

Interactive comment on “Development of a new Long Path Absorption Photometer (LOPAP) instrument for the sensitive detection of NO₂ in the atmosphere” by G. Villena et al.

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We would like to thank referee #1 for his/her comments that helps us to improve our manuscript. Below are the answers to the referee's comments:

Referee: 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.

Response: First of all, for extremely clean conditions for which NO₂ levels are in the very low ppt range as mentioned by the referee, PAN concentrations will typically not reach some hundred ppts. For example, at Neumayer station in Antarctica for which

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very low NO_x levels <10 ppt are often observed, PAN levels around 10 ppt have been reported (Weller et al., JGR, 107, 4673, 2002). In this case, interferences of 0.5 % would not be a problem. In addition, in the manuscript only an upper limit of <0.5 % is specified in Tab. 3, thus the true PAN interference may be much lower. We could not determine a lower limit, since this interference was determined by comparison with an FTIR in a complex photochemical mixture, in which PAN was also formed besides other products. Caused by the low precision of the FTIR and the complex reaction mixture only the upper limit of <0.5 % could be determined.

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

Answer: In page 1754, line 10 is written that “some of them”, i.e. not all the spectroscopic techniques are expensive, suffer from great experimental efforts and have expensive system components. But since one may misunderstand the second part of this sentence, we will modify in the revised manuscript to: “. . ., with some of them reaching very low detection limits (REMPI, LIF). However, several of these techniques (e.g. REMPI, pulsed CRDS, DOAS) suffer from great experimental efforts, expensive and complex system components.”

Referee: Production and loss of NO₂ in inlets has plagued many measurements. The accuracy of the calibration should be referenced to standards at the inlet. Most 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 unstable. That is easy to check, for example by absorption spectroscopy.

Answer: On page 1767, lines 1–9 we mentioned that one advantage of the LOPAP

instrument is the calibration by liquid nitrite standards, because their accuracy (1%) is higher than that of NO₂ gas standards (typically 5 %). This is an important point which we still would like to highlight. In addition, in our experience, NO₂ gas standards often deviate more from the nominal concentration given by the manufacturer than the stated accuracy, especially after some months. In addition, the NO₂ level in a calibration gas bottle also depends on the temperature of the bottle, caused by adsorption effects (e.g. when working in a field container at 35 °C. . .). Since not all groups will have the opportunity to check the NO₂ concentration by absorption spectroscopy during a field campaign, at least for the LOPAP instrument the liquid calibration is much more accurate than the use of a NO₂ calibration standard. The referee also mentioned losses of gases in inlets typically used. This is a very important point, since these losses depend on the quality of the inlet lines used (material, age, adsorbed soot, filter if used, etc.). Thus, the concept of the LOPAP is not to use any inlets, but to directly place the temperature controlled stripping coils in the atmosphere of interest and to pump the sampling solution after reaction with NO₂ to the detection unit. This avoids any line artefacts, which thus need not to be quantified here. But this point is independent from the accuracy of NO₂ calibration gases which we mentioned in the manuscript.

Referee: 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.

Answer: Since this instrument was yet not used under remote conditions, we do not have such plots available. In addition, why should an intercomparison <40 ppb be not demanding. Many potential interfering NO_y compound like PAN, nitrates, etc. are formed under photochemical conditions in the atmosphere, leading to high disagreement in intercomparison studies at high pollution level (see e.g. Dunlea et al., 2007). If for Figure 10 only the NO₂ data lower than 5 ppb is used only a very few points fall into this range. Using the data <6 ppb results in a correlation: LOPAP = 0.998x ECO +0.19

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ppb, which is of similar quality than the correlation shown. The ABS against NO₂ plot shown Figure 7 should not only show the linearity of the calibration but also the linear range in which the LOPAP can be used. Thus, we also would like to leave this plot as it is.

Referee: The authors should discuss the possibility of other interferences more comprehensively. In 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.

Answer: The more complex interferences were studied in the photochemical experiment which is only shortly summarized on page 1771. An excellent agreement was observed for these conditions, for which hundreds of products, including those mentioned by the referee, were formed. However, since a more detailed explanation of these experiments is necessary, which would be beyond the scope of this paper, we decided to publish more details about these experiments including problems of commercial instruments in another manuscript, which we recently submitted to Atmos. Meas. Tech. Discuss.: "Interferences of commercial NO₂ instruments in the urban atmosphere and in a smog chamber".

Referee: 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?

Answer: The ratio between the intensity where the absorption is measured under zero

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air, $I(0)$, and the intensity at the reference wavelength, $I(\text{ref})$, i.e. the zero raw absorbance data is indeed depending on the parameters mentioned above. However, the changes are small (ca. 10 ppt/day), typically linear with time and can be followed by regular zero measurements, the periods of which depend on the NO₂ level (i.e. for very low NO₂ level every 4 h, for urban conditions every 8-12 h recommended). The reagents (10 l containers) have to be renewed ca. every three weeks after continuous operation of the instrument and certainly a new zero correction and calibration is necessary than. The precipitation of NEDA also leads to a reduction of the light intensity of the diodes. But also these changes are slow and need some increase of the light intensity of the diodes may be every week (without changes in the zero absorbance signal, thus can be done during the measurements. . .). Since the intensity of the pulsed diodes can be varied over 2 orders of magnitude, this needs no maintenance work. Only after every ca. 1 year the AF tubes need to be cleaned by flushing for some min with diluted NaOH solutions. Thus, all these things are not problematic for the typical operation of the instrument in campaigns.

Referee: 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.

Answer: The calibration is done under zero air (one point) and then the feed tube for the sampling solution is placed in a flask with a nitrite standard of known concentration diluted in the same sampling solution. Thus, there is no "infrastructure" necessary.

Referee: 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?

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Answer: The material of the stripping coil is glass, which we will mention in the revised manuscript. Thus, typically all the glass coil is homogeneously covered by the liquid. If the coil gets dirty e.g. by adsorption of hydrophobic soot after operation for some weeks under polluted conditions, it has to be cleaned by flushing with a diluted NaOH solution. The residence time of the liquid in the stripping coil is ca. 2 min and thus, it is one important factor for the overall time response of the instrument of 3 min.

Referee: For the reported accuracy of 10% which is much larger than 0.5% precision and 1% nitrite 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?

Answer: The given accuracy is including the errors of the undiluted nitrite standard, but also errors during the dilution of the standard for calibration (typically three dilution steps necessary). In addition, it includes errors in the measured gas and liquid flow rates, the loss of NO₂ in the HONO/ozone scrubber, the sampling efficiency and the error of the Saltzman factor, the latter of which is the highest uncertainty yet. The Saltzman factor is calculated from the difference between the gas concentration of NO₂ by a gas calibration standard and the concentration determined from the nitrite calibration. Whereas the overall error of the nitrite calibration is only 5 % the error of the NO₂ calibration standard is ca. 10 %. If in the future a more accurate NO₂ calibration standard is available, leading to a more accurate Saltzman factor, the overall accuracy of the instrument can be further reduced.

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