**Atmospheric
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Discussions**

Interactive
Comment

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.

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We would like to thank referee #3 for his/her comments and suggestions that help us to improve our manuscript. Below are the answers to the referee's comments:

Referee: Page 1754, line 11: Some of the techniques listed do suffer from "great experimental efforts," but not all of them. Several of the detection principles, such as cavity attenuated phase shift spectroscopy (CAPS), are quite simple. They may even be arguably simpler than a method based on a series of solution phase reactions as described here.

Answer: The referee is correct, there are also some other recently developed spec-

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troscopic methods which may be simpler than e.g. REMPI, DOAS or pulsed CRDS methods, which we had in mind when we wrote this sentence and for which this statement is still true. On the other hand these new methods still do not reach the very low ppt detection limit obtained e.g. by the REMPI method (and the LOPAP), see sentence before. We modified this section 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: Page 1756, line 9: 4% of the NO2 is removed in the first scrubbing phase. How well is this quantified? Does it vary?

Answer: This value was determined by sampling of a NO2 calibration gas mixture at a constant concentration and changing the scrubber solution (sulphanilamide (10 g/l), Indigo trisulphonate (0.6 g/l)) in the first stripping coil by a new scrubber solution with the same composition except without Indigotrisulphonate. For the latter solution only insignificant NO2 loss (<0.1 %) was observed in our HONO LOPAP instrument, for which a similar solution is used to sample HONO. The loss was measured several times and was found to be stable (4 +-0.5 %).

Referee: Section 3.1: The section describes how two critical parameters, the sampling efficiency and the Saltzman factor, vary with the reagents. However, it is not clear how either parameter is actually measured. A precise description at the start of this section describing how the amount of NO2 absorbed in the first coil (sampling efficiency) and the amount of dye per NO2 absorbed (Saltzman factor) must precede the section. In particular, how are these determined independent of one another?

Answer: The sampling efficiency is determined from the ratio of the NO2 signals in the NO2 channel (coil 2) to the one in the interference channel (coil 3) assuming that the Saltzman factor is similar in both coils, which is reasonable, since the same sampling solution is used in both coils. In contrast, the Saltzman factor is determined from the

ratio between a known NO2 concentration (calibration gas) and the signal obtained in the NO2 channel taking into consideration the loss of NO2 in the HONO/O3 scrubber (-4%) and the loss of NO2 by incomplete sampling in the NO2 channel (loss of 5 and 3 %, respectively, depending on the coil used, see text). However, the definition is already given on page 1760, lines 10-14, which we slightly modified for clarification: "In the present study, the sampling efficiency is defined as the proportion of NO2 incorporated in the second stripping coil (Channel 1) with respect to the total quantity of NO2 entering this coil. The Saltzman factor is calculated based on the proportion of the generated amount of dye in channel 1 with respect to the quantity of NO2 absorbed in this channel".

Referee: Page 1763, line 3 (and Table 1): The new coil leads to better time resolution and higher sampling efficiency of 97% - does this 97% take into account the 4% loss in the first coil? Should it better be expressed as 93%?

Answer: The sampling efficiency optimized in the present study (i.e. finally 97 %) is independent from the loss of NO2 in the HONO/ozone Scrubber (4 %) and should be separately specified. But the referee is correct, the total amount of NO2 entering channel 1 is only 93 %.

Referee: Section 3.2: How was the NO2 on the x-axis of Figure 7 measured? The discussion suggests that NO2 gas standards are unreliable, so presumably the independent NO2 standard was something other than NO2 from a standard mixture. Also, if I understand this correctly, the calibration against a nitrite standard does not take into account the entire instrument response, but only the derivatization step. The sampling efficiency, given here as a single number (97%), is not part of this calibration, nor is the loss in the first scrubber. Is there a variation in NO2 sampling efficiency or the NO2 loss in the first stripping coil that must be calibrated (or assumed) independently of the nitrite calibration standard? More details on these points would be helpful to the reader.

Answer: The instrument is not calibrated by a gaseous NO2 standard, but by the liquid nitrite standard. Thus, Fig. 7 should only demonstrate the linearity and the measurement range of the instrument (which is independent on the accuracy of the NO2 calibration gas used here). In contrast, in Fig. 7 we used a gas standard and changed the concentration by dilution with known amount of synthetic air. Thus, the concentrations given on the x-axis are theoretical NO2 concentrations calculated from the calibration gas concentration and the know dilution ratio. If a gas calibration were used (ABS against [NO2], see Fig. 7), than no correction of the loss of NO2 in the HONO/ozone scrubber, of the sampling efficiency and the Saltzman factor would have been necessary. However, caused by the problems with the accuracy of the calibration gas, we prefer the liquid calibration, for which the 3 correction terms are necessary.

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