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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 #2

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General comments:

This manuscript describes a new measurement methodology for NO2 in ambient air. It is based on the considerable prior experience of this research group with LOPAP techniques, which are best known for their application to HONO. The instrument is highly sensitive (2 pptv), and has a reasonable dynamic range (up to 300 ppbv). It would therefore be useful in a wide range of applications, from polluted to more remote areas. The time response is rather slow (3-6) minutes, making this instrument applicable mainly to measurements from ground locations. However the authors state that its design is simple enough to make it relatively versatile and easy to deploy.

The authors consider the specificity of the instrument against various interferences. As long as HONO and O3 are effectively scrubbed at the inlet, the instrument appears to be reasonably specific to NO2. This scrubbing efficiency, and the passing efficiency for NO2 through the initial scrubber, would appear to be the most serious analytical concern for this instrument. The authors present a detailed set of measurements of the scrubbing efficiency and less detail about the passing efficiency. The ambient intercomparison data against a commercial instrument are consistent with the quantitative NO2 measurement, however.

The paper is comprehensive and requires only a few additional details to be added. In particular, the methodology for independent NO2 measurements in laboratory validation studies were not specified (or if they were, not clearly enough stated). This and other comments appear below in the specific comments section. The authors should address these minor comments prior to acceptance.

Specific comments

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.

Page 1756, line 9: 4% of the NO2 is removed in the first scrubbing phase. How well is this quantified? Does it vary?

As a side note, this type of scrubber would seem to be useful for photolytic converter based chemiluminescence instruments as well since these are prone to interference from HONO.

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?

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%?

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.

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