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Atmospheric Measurement Techniques Discussions

Interactive comment on "A novel instrument for measurements of BrO with LED based Cavity-Enhanced Differential Optical Absorption Spectoscopy" *by* D. J. Hoch et al.

D. J. Hoch et al.

ulrich.platt@iup.uni-heidelberg.de

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Dear Editor,

We like to express our gratitude to the referee for valuable comments and questions on the paper with the title 'A novel instrument for measurements of BrO with LED based Cavity-Enhanced Differential Optical Absorption Spectroscopy'. We are confident that we answered all questions raised and that we were able to provide a revised version of our manuscript on the basis of these comments.

All changes are identified in the revised manuscript by page number, p, and line num-

ber, l, as used by the referee as well. Additional comments and explanations are in bold letters.

Comments: - The abstract should indicate that the detection limits refer to single concentrations and not mixtures of the four analytes: "In laboratory studies, BrO as well as HONO, HCHO, O3, and O4, could be reliable determined at detection limits of 20 ppt for BrO, 9.1 ppb for HCHO, 970 ppt for HONO, and 91 ppb for O3 , for five minutes integration time [with single absorbers], respectively."

In fact, the detection limits are determined in experiments where more than one absorber was present in the smog chamber. For example, simultaneously measured high BrO and O3 concentrations are shown in Fig. 13. The detection limits given refer to Table 5. The detection limits given in the abstract are realistic for measurements of mixtures and would be even better if only a single absorber was present. Therefore, the abstract is left unchanged.

- NO2 is the strongest absorber in this spectral region for most of the atmosphere, but it is not mentioned in the manuscript. It's potential detection limit and interference with retrievals of BrO should be discussed.

An estimation for detection limit of NO2 is given in Table 5. NO2 can be a strong absorber depending on concentration and path length, but its potential to interfere with the detection of BrO is minor since differential optical cross-section of NO2 is relatively small (less than 1/100 than that of BrO) in the wavelength range where BrO is evaluated. Furthermore, one of the major – and well known – advantages of DOAS is its capability to separate the absorption of different molecules in mixtures. The simultaneous and reliable measurement of the concentrations of different gaseous components is demonstrated in many previous studies (e.g. Platt and Stutz 2008 and references therein). We included the following text on p6066 l 24:

In Table 5, the detection limits for the measured trace gases for the two different mirror sets and different integration times are given. An estimated detection limit for NO2

of 3.6 ppb at an integration time of 3 minutes is given as well. The differential NO2 absorption (~3*10^-20 cm^2/molec) in the wavelength range between 325nm-360nm is relatively weak compared to BrO (~3*10^-17 cm^2/molec), but concentrations could differ by 3 orders of magnitude in nature and thus be in the same magnitude. Nevertheless, it has been shown that NO2 and BrO can be detected simultaneously and reliaby by DOAS before (Platt and Stutz, 2008, Mahajan et al., 2009, Pöhler et al., 2010).

We added the following reference: Mahajan, A. S., Oetjen, H., Lee, J. D., Saiz-Lopez, A., McFiggans, G. B., Plane, J. M. C.: High bromine oxide concentrations in the semi-polluted boundary layer, Atmos. Environ., 43, 3811–3818, doi: 10.1016/j.atmosenv.2009.05.033, 2009.

- Section 4.2 lines 4 – 16 describes the method for calculating the detection limit and corrections to this detection limit. Several corrections to the detection limit are discussed. It would strengthen the paper to report the 1-sigma precision for the retrieved concentration timeseries of a constant concentration of BrO (and other species), since the authors likely already have this data.

We appreciated the suggestion of reporting the precision for constant BrO concentrations. However, in our chamber experiments conducted so far the lifetime of BrO towards ozone was relatively short (see Fig. 13), and thus the BrO level was not constant for a sufficiently long time to calculate the precision. Experiments with controlled Ozone concentration could, in principle, be done in the future, but would require further development of the chamber set-up (e.g. flow regulation system for ozone). Thus, the suggested 1-sigma precision could not be determined requiring no changes to the manuscript. The determination of the detection errors are described in Sect. 4.2 instead.

- Pg 6070 lines 19 – 25: “Due to its compact size and low power consumption it is possible to apply the BrO CE-DOAS-instrument – besides in reaction chamber investigations – also in field studies with batteries even if other electrical power is not available.

To to our knowledge this instrument is the first mobile cavity based BrO instrument in the UV wavelength range, which is applicable to field measurements. As mentioned above two other CE instruments exist for the detection of BrO (Chen and Venables, 2011; Grilli et al., 2012), but their field application seems to be limited due to size and power consumption.” This paragraph states that this instrument can be used for field measurements, but the ability to simultaneously measure multiple absorbers at atmospherically-relevant concentrations isn’t demonstrated in the paper. It should be edited to indicate that field measurements with UV LEDs may be possible in the future.

As mentioned above we did in fact investigate the presence of several absorbers simultaneously. During the described experiments, the optical densities of potentially interfering absorbers were even higher than typically present in the atmosphere. We have edited the text as follows:

Page 6070 lines 19 – 25: . . . . .To to our knowledge this instrument is the first mobile cavity based BrO instrument in the UV wavelength range, which is applicable to field measurements. Thus in-situ measurements with UV LEDs especially of BrO are possible in the future.

In order to clarify our approach, we added to the captions of Fig. 5. and Table 5. Derived detection limits are based on measurements of gas mixtures (cf. Sect. 4.2).

- The prior reviews were concerned with the novelty of these results. In this revised version, the authors have added “novel” to the title. It is not needed.

We agree with the Referee and deleted "novel" in the title.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/6/C2844/2013/amtd-6-C2844-2013-supplement.pdf

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