

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

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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-

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

Title: “Spectroscopy” instead of “Spectroscopy”

Corrected.

p6049 l1: make “3” a subscript of “O3”

Corrected.

p6049 l28ff: Although the authors are surely correct that CRDS instruments which apply a single wavelength are limited with respect to their specificity, I would not call it a shortcoming. It only limits their applicability.

We edited p6049 l28ff as follows:

A limitation of most CRD instruments is that any extinction (absorptions or scattering) beside that of the investigated trace gas at the applied wavelength leads to interferences and must be avoided. Thus measurements at spectral ranges, where several molecules absorb cannot be used (e.g. the UV spectral range due to O₃ and NO₂ absorptions). Additionally this requires the removal of aerosols and thus typically demands closed resonators with aerosol inlet filters. Moreover, this approach introduces the risk of trace gas loss as well as possible chemical reactions on the inlet and filter.

p6050 l1-3: The authors refer aerosol extinction only to absorption mentioned in the sentence before. Please rephrase.

See edited paragraph above.

p6050 l3: What chemical reactions are the authors thinking of, when they state that a closed resonator is a risk? Please specify.

We added the following remark on p6030 l3: (e.g. conversion of HOBr to Br₂ (Neuman et al., 2010), or BrO self-reaction (Liao et al., 2011)).

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p6050 I23-25: This statement is contradicting the statement on p6051 I1-2, where the authors state the system by Grilli et al. is suitable to perform field measurements. Please make this consistent.

The instrument described by Grilli et al., can be transported into the field. But it requires a laboratory providing a sufficiently constant temperature, mechanical stability and power supply required by the laser-optics. Therefore, the applicability of the instrument described by Grilli et al. is limited.

The sentence starting p6050 I23-35 is changed to: This means that there is a lack of in-situ instruments allowing mobile measurements of BrO radicals in the field without requiring laboratory infrastructure.

We removed 'transportable' on p6051 I1-2.

p6051 I1-14: The authors mix up statements about CIMS instruments and the CE instrument by Grilli et al. in this section. It would be much easier to read, if this was clearly separated.

Although we think that comparison of different techniques for the detection of BrO is not the point of our manuscript, we agree that a mix of statements on CIMS and CE instruments might be confusing to the reader. We changed the paragraph starting on p6050 I26:

The mode-locked frequency-doubled cavity-enhanced spectrometer described by Grilli et al. (2012) has a 7m Teflon inlet tube. Although the instrument provides BrO detection with remarkable good detection limits of 1.7 ppt at a time resolution of 30 s, the possible effect of inlet losses was not investigated so far. The authors state undetectable BrO losses within the relatively large concentration fluctuations of up to ± 12 ppt. This result does need further confirmation, since a characterisation of the inlet system is still missing for CE-spectrometers as described by Grilli et al. (2012). Besides cavity instruments, Chemical Ionization Mass Spectrometers (CIMS) are capable of indirect

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BrO detection, but complex sample preparation and calibration is needed (e.g. Neuman et al., 2010; Liao et al., 2011). This limits the application of these instruments for field studies, where low power consumption, simple operation, and a lightweight setup is required. Additionally, loss or chemical conversion of highly reactive compounds (e.g. BrO or HOBr), on instrument and inlet surfaces occur and can even result in a complete loss of BrO, which can influence the indirect detection of BrO with CIMS instruments (Neuman et al., 2010). Nevertheless, it was demonstrated by Liao et al. (2011) that reliable BrO concentrations can be provided by an optimised and very short inlet CIMS instrument. These measurements were found to be in good agreement with a well established long-path DOAS system (Liao et al., 2011).

p6051 I12: Better say "by an optimized CIMS instrument with a short inlet".

We agree with the referee and changed the manuscript accordingly.

p6052 I11: Please add the species that were measured by the White-cell DOAS system.

We included the list of species by changing the text on p6052 I11 as follows:

Also, we compare the CE-DOAS results with an established White-System DOAS for detection of BrO, O₃, HCHO, NO₂, HONO, O₄, OClO, SO₂ and a chemiluminescence O₃ monitor.

p6053 I2: I assume that lambda does not belong to the subscript:

We agree with the Referee and set the lambda dependency in normal case.

p6057 I6: Why is it important to detect ozone? The detection limit is far away from being useful for atmospheric measurements. Please justify your statement.

We think that the detection limits for ozone of 91 ppb (five minutes integration time) and 59 ppb for integration times of 81 min or less, are sufficient for many laboratory studies. Even if the detection limit seems to be very high, it allows a comparison of measured

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O3 concentration with other techniques at such high concentrations and thus allows to double check e.g. the instrument calibration.

p6057 l15: There is one more right parenthesis than left ones.

We removed one parenthesis after 0.991.

p6057 l21: "for" is not needed here.

Deleted "for" as suggested.

p6059 l18: "control" instead of "controll" p6059 l21: "receives" instead of "receive"

We made both changes as suggested.

p6060 l1: Please give a typical number for tau1. How stable is tau1 over time? Please state more precise what determines tau1 instead of giving a general description as "electro-optical" decay.

We agree with the Referee that more information needs to be given here and applied the following changes to the manuscript:

A typical value for tau1 is 100ns and it is determined by the rise time of the pulse electronics of the LED and the rise time of the LED output itself.

p6060 l1-12: I do not think that this part is appropriate for a section named "Software". It does not describe a software, but gives information how useful (or not) the CRD mode of the instrument is.

We agree with the reviewer and change the section - title to: "Data recording and Cavity Ringdown calibration"

p6061 l3-4: It sounds trivial that a change in the path lengths in the different set-ups is useful to have different cavity lengths. Please specify precisely why it is useful to have different cavity lengths.

We removed this sentence.

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p6068 l1: "is" instead of "are"

Corrected.

p6068 l17-18: Regarding the high detection limits for O3 and HONO I do not see the advantage of being able to measure different species simultaneously. Except for laboratory experiments with exceptionally high concentrations, the ability of the instrument to detect O3 and HONO will not be useful. Please justify your statement.

Although the applicability might be limited to more polluted areas regarding the detection limits of O3 and HONO (see also statement above) we see high potential for improving the detection limits in the future. Therefore, we added the following sentence on p6068 l17-18:

Although, it is limited to areas with high concentrations and laboratory studies at the current state.

p6068 l25: Please add the time resolution of the DOAS White system, so that the reader can compare numbers.

The sentence on p6068 l25 now reads:

[. . .] 50ppt for a time resolution of 4 minutes(Buxmann et al., 2012).

Fig. 11/12: Error bars of the WS-DOAS in Fig. 11 and error bars of the CE-DOAS in Fig. 12 are much larger than the scatter in the data suggest. Please discuss reasons why this is the case and discuss the influence of the unrealistic large error bars on the fit results, since the fit procedure takes error bars in both coordinates into account.

The error of the WS-DOAS is based on the DOAS fit and a 2.5-sigma error of a single fit error is shown here as described in section 4.2 on page 6066. Especially in Fig.12 the scatter of the data justifies the large error of the O3 detection. The error estimation according to (Stutz and Platt, 1996) includes also systematic measurement errors (and not only statistical errors), e.g. due to remaining spectral structures in the residual

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or imperfect literature absorption spectra. Thus, the scatter of the data can be much smaller than the statistical measurement error.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/6/C2848/2013/amtd-6-C2848-2013-supplement.pdf>

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 6047, 2013.

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