

Author comment on

Interactive comment on “A Cavity-Enhanced Differential Optical Absorption Spectroscopy instrument for measurement of BrO, HCHO, HONO and O₃” by D. J. Hoch et al.

Anonymous Referee #1

We would like to thank Referee 1 for the extensive review and the helpful comments which helped to improve the quality of our manuscript. Although we do not agree with all points raised by the Referee, we reply to them and made most of the requested modifications. Furthermore, we included additional calibration measurements. In the following we answer to the given points.

Referee 1: The authors describe the application of CE-DOAS for BrO using an LED with an output wavelength between 325 and 365 nm. The instrument mainly differs in the wavelength range of the light source, but is otherwise similar to instruments described by the same group before.

Answer: This is a very general comment. One could always say that new instruments are “in principle the same” as previous ones because, typically, they have several features in common. In particular, the Referee appears to greatly underestimate the effort needed in order to extend the wavelength range of a cavity into the UV spectral range.

We included the following text: “Compared to instruments designed for the VIS/IR wavelength range, Rayleigh scattering and parasitic mirror losses become important in the UV and thus decrease the achievable maximum path length. Both effects are discussed in this paper.” at p3082 l11.

Furthermore, the influence of the absorption in this spectral range on the measurements is described in subsection 4.1.

Referee 1: Although the extension of cavity-based absorption techniques to this wavelength region is of importance, in order to detect compounds which have no specific absorption features at longer wavelengths, the novelty of the instrument is rather small. Experiments described in this paper, which were conducted at conditions not relevant for atmospheric measurements, are only motivated by testing the instrument.

Answer: We strongly disagree with the Referee and inserted the following points for clarification:

“This is a novelty because there is no cavity based instrument in this wavelength range which is applicable to field measurements.” inserted at p3096 l9

inserted at p3094 l19:

“We developed the first LED based CE-DOAS detection of BrO in the UV-wavelength range from 325 nm to 365 nm. Due to the low power consumption of the light source, the instrument can be applied to field measurements with limited or unstable power supply. The achieved BrO detection limit is 11 ppt using a time resolution of 81 min per measurement.”

We agree with the Referee statement “...a cavity instrument at this spectral range is of large interest, as many important trace gases can only be measured in this spectral range.”

Referee 1: The main result of this paper is the determination of the detection limits of the instrument for species that can be detected in this wavelength region based on the residual

structure of the DOAS fit. The majority of these species, however, can be detected by other instruments with much higher sensitivity.

Answer: This comment of the Referee requires clarification. While some of the species might be detectable by other, specialized instrumentation the great advantage of our CE-DOAS instrument is the capability to detect several species with the same instrument. We included the following text:

“The advantage of the new UV LED CE DOAS is that it is capable to measure different species (e.g. BrO, O₃ and HONO) simultaneously and reliably. Additionally it is a remote sensing instrument and thus measuring the trace gases in comparison to most other in-situ instruments directly in the atmosphere without any losses or reactions on inlets, filters or walls.” inserted at p3094 l23

Referee 1: The paper would for example benefit, if there was any comparison with other reference instruments to show that measurements are reliable.

Answer: We agree with the Referee and added a comparison with a White-System DOAS and an ozone monitor.

Inserted at p3080 l16

“Comparison with established White-System DOAS and O₃ monitors demonstrate the reliability of the instrument.”

Inserted at p3082 l15

“An intercomparison with an established White-System DOAS and a CL monitor for ozone detection are presented.”

Inserted paragraph at p3092 l18:

“3.2.5 Comparison of the CE-DOAS with a White-System DOAS and an ozone monitor

During experiments with a simulated salt pan [Buxmann et al.2012] at the Atmospheric Chemistry Research Laboratory, University of Bayreuth, Germany, in the low-temperature aerosol simulation chamber (LOTASC) [<http://www.eurochamp.org/chambers/lotasc/>] a comparison between the CE-DOAS and a White-System (WS) [White 1976, White 1942, Ritz et al. 1993, Volkamer 1996, Volkamer et al. 2002, Hak et al. 2005] as well as the CE-DOAS and an chemiluminescence-ozone monitor (CL, Bendix-UPK8002) was performed. The cylindrical chamber, made of Teflon foil (FEP 200A, DuPont, thickness 0.05 mm) with a diameter of 1.33 m and a volume of 3500 l has been described in detail by Siekmann [2008], Bleicher [2012] and Buxmann et al. [2012]).

The LOTASC was kept at a pressure slightly above atmospheric pressure in order to prevent leaking of room air into the system. This was controlled by a bypass system. The dilution rate, replenishing the loss by sampling and other outlets, was of the order of $3 \times 10^{-5} \text{ s}^{-1}$, which corresponds to about 4 l/min zero air input [compare Buxmann et al. 2012 and Buxmann 2012 Dissertation]. Therefore the purge flow of the CE-DOAS mirrors was included.

During the intercomparison experiments the WS had a base path of 2 m and an aperture of F/25, with a total light path of 288 m diagonally arranged through the chamber, whereas the CE-DOAS light path was horizontally arranged with a mirror distance of 1.33 m. In order to determine the absolute light path in the cavity, O₄ measurements were carried out, as described above. For that purpose an additional tube was mounted in between the resonator inside the smog chamber. The maximal path length at 346.3 nm was 816 m. A sketch of the experiment set up is shown in Fig. 9. These experiments were described in detail in Buxmann (2012) and the results are described in Sect. 4.”

Inserted at p3093 l11

“4.2 Comparison results

The BrO time series (fig. 10) shows a very good agreement between the CE-DOAS and the WS-DOAS systems for mixing ratios from below the respective detection limits up to 400 ppt;

The slope of the BrO mixing ratios measured by each instrument is 1.06 ± 0.07 using a bivariate weighted fit as suggested by Cantrell (2008) to obtain a correlation coefficient of $r^2 = 0.95$. The agreement of HCHO of the two multireflection systems is remarkably good as well, with $r^2 = 0.998$ and a slope of 0.97 ± 0.03 for values up to 1 ppb, using again the bivariate fit (fig. 11).

The correlation plot for ozone furthermore shows (Fig. 12) a very good agreement between the CE-DOAS and the CL ozone monitor with a slope of 1.11 ± 0.08 and $r^2 = 0.92$, even though the CE-DOAS measurement spectral range is not optimized for ozone measurements. The excellent agreement between the two multireflection systems (WS and CE-DOAS), measuring at different light paths, demonstrates the accuracy and reliability of the newly developed CE-DOAS instrument. Integrity of operation is evident by the good agreement with the ozone monitor, which takes in air from a single location close to the chamber wall. This intercomparison of the instruments also demonstrates the rapid mixing of the chamber air within a timescale of 120 seconds (average time resolution of the instruments).“

Inserted at p3095 l3

“For validation an intercomparison between the CE-DOAS and a White-System (WS) DOAS as well as between the CE-DOAS and a chemiluminescence-ozone monitor (CL, Bendix-UPK8002) was performed. Excellent agreement between the two multireflection systems (WS and CE-DOAS), measuring at different light paths and good agreement with the CL-ozone monitor, demonstrates the reliability of the newly designed CE-DOAS instrument.”
Instead of:

“For validation of the achieved measurements we plan a comparison campaign with an active DOAS instrument in combination with a well established multireflection cell (White(1976); Ritz et al.(1993); Volkamer et al. (2002); Hak et al. (2005); Buxmann et al. (2012); Ofner et al. (2012)) at Bayreuth.”

Referee 1: On the one hand the performance of the instrument in the current status is only applicable for atmospheric measurements of very large BrO concentrations with a sufficient time resolution as stated by the authors in the conclusions and on the other hand the potential advantages of CE-DOAS such as specificity and insensitivity to aerosol extinction are of less importance for laboratory studies. The status of the instrument development seems to me in an early state. The applicability of the instrument for atmospheric measurements except for some special cases when exceptional large BrO concentrations are expected is not clear from measurements shown here. No new concepts are applied, which would justify publication of this state of the instrument development. The experiments shown in this paper have the character of technical tests, which only demonstrate that the instrument can detect BrO, but no analysis of the quality of measurements except for an estimation of the instrument precision is done.

Answer: We think that the points given by the Referee do not acknowledge our development properly. The instrument was designed and optimized especially for measurements in the UV- spectral range from 325-365nm. The difficulty in this wavelength range is that the output power of UV-LEDs are still several orders of magnitude lower than that of LEDs in the visual wavelength range, although they show advantages compared to other light sources for the UV range like Xe-lamps (comparison see at Referee 2). Furthermore, the mirrors in this wavelength range cause some problems like relatively high absorption, as discussed below, which might be solved in future. To overcome these problems, extensive constructions, optimizations and measurements were made to deal with these problems as well as possible, and very good results were achieved. We do not agree with the statement that this instrument has no application for measurements. First it has in most cases a better measurement accuracy than available White System and is thus ideally applicable for

chamber experiments, second there are measurement locations where BrO concentrations are well above the detection limit of the presented instrument (see manuscript p3096 l11-14). Even if other instruments with better detection limits exist, they are either not in-situ instruments or insufficiently mobile to perform measurements e.g. in a volcano or above a salt pan.

Referee 1: In the conclusions, the authors give a list of future improvements and planned comparison measurements. The paper would have benefited, if at least part of the planned work had been included in this publication. I encourage the authors to resubmit the paper when the instrument development will be finished.

Answer: We cannot completely agree. The performed comparisons are included in the revised manuscript. The list is given as an outlook on potential improvements which may be realistic to be applied in the next years. This list may also help other groups to benefit from our experiences in the future. Thus, we think the Referee's criticism is not justified. We also do not agree with the statement that a publication may only be possible once all improvements are made. Following this argument a technical publication would never be possible. There are always possible improvements and thus a technical development is always an ongoing process. The instrument will be continuously improved by our research group in the future. Nevertheless we do believe that the results of this publication are meaningful. We would like to report on the present achievements and therefore we disagree with the comment to resubmit the paper after the instrument development has been finished.

Referee 1: In addition, major changes and additions would be required concerning the following specific points:

- The performance of the instrument in the current state of its development is mainly applicable for laboratory studies such as chamber studies with large concentrations as mentioned by the authors. This limitation of the instrument should be more clearly indicated in the title and abstract.

Answer: We disagree with this statement as replied above.

Referee 1:• p3081 l17: The list of references is not appropriate, because there are many other studies, which have improved the CRDS technique for its application in atmospheric research.

Answer: Ring down measurements are not that relevant here. From our perspective it is not appropriate to compare CE-DOAS with CRD, because CE-DOAS has an important advantage for application to atmospheric measurements, like simultaneous detection of several trace gases with an open path cavity even if aerosols are present. These measurements are not possible with a closed CRD system with aerosol filter due to wall losses.

Referee 1:• I miss a comparison of the performance of the described instrument with previous measurement techniques, in order to give the reader an idea what can be achieved with the CE-DOAS instrument. Because this instrument seems mainly applicable for laboratory studies, this should include also instruments used in other laboratory studies such as the CRDS instrument applied in a study by Sakamoto J. Phys. Chem. A 2009. The introduction should more clearly state the motivation why CE-DOAS in this wavelength range would be advantageous compared to other techniques used to measure BrO. The discussion of results should include a comparison of the achieved performance to other instruments and consequences for its applicability.

Answer: We thank the Referee for this suggestion and accordingly include a comparison with a White-system and a CL monitor for ozone detection. (see above)

Referee 1:• In the “method” section, the authors repeat the data evaluation of CE-DOAS described by Platt et al. 2009. This could be significantly shortened, because the equations are not helpful to understand the instrument without having read the paper by Platt et al. It would be sufficient to refer to Platt et al. and to give a short description of the principles.

Answer: We agree with the Referee. The method section is now reduced to a minimum.

Referee 1: In section 2.4 I miss a reason why the authors used one or the other method to derive the correction for light path reduction. Why was the second method not applied for measurements of single compounds?

Answer: The first method was applied because the second method is less accurate as it requires an absolute stable intensity. However, the first method becomes very complicated and calculation intensive if several absorbers exist.
See at p3086 l9

Referee 1:• p3087 l15: The authors mention that ozone acts as an interference, whereas the instrument is regarded as an ozone detector in the rest of the manuscript. Please make the arguments consistent. If ozone is regarded as an interference the consequences for the detection of BrO needs to be discussed.

Answer: We agree that this point should be clarified with the following text:“, but still appropriate to detect O₃.” Inserted at p3087 l15

Referee 1:• In the “Software” section it is stated that the ring-down trace was fitted to an exponential function with two decay constants, one of which refers to electronics. Why is this necessary? Is the electronics too slow to follow the decay of the light intensity? If this was the case, why was not an appropriate electronics chosen?

Answer: Electronic decay time is mainly characterized by the LED capacity which cannot be changed by the electronics. The electronic circuit itself is already well-optimized for fast decays.
The second constant just accounts for this decay time.

Referee 1: This part should be moved to a different section, because this clearly is not a description of the software.

Answer: As the fitting is a pure software issue we do not see the point that it would be more appropriate in another section.

Referee 1:• I do not really understand the set up of the instrument in the chamber. Was the optics part also sealed against the chamber between the optics? If this was the case, how was this achieved and what consequences has this for the measurements, because some window with additional optical properties would be required? If there was no sealing how did the purge flow of the mirrors compared to the flow of the absorber? Was dilution of the absorber by the purge flow taken into account during the long integration time?

Answer: No seal against the chamber was present because it is an open path instrument. The purge flow of the mirrors was 1 l/min during all experiments (compare chapter 3.2). The chambers A, B and C were kept in pressure equilibrium with the laboratory. To avoid an airflow beside the mirrors and thus cause contaminations caused by slight overpressure of the chambers, the purge flow of the CE was even needed. Furthermore, the chambers A, B and C had two open outlets as indicated in Fig.2 to avoid over pressure. In case of the LOTASC Teflon chamber the mirror purge flow was connected to the overall zero-air flow. LOTASC was kept slightly overpressurized, in order to prevent leaking of room air into the system, which was controlled by a bypass system. The dilution rate was in the order of $3 \times 10^{-5} \text{ s}^{-1}$, which corresponds to about 4 l/min zero air input [compare Buxmann et al. (2012) and Buxmann (2012)].

For clarification we included the following text:

p3090 I11 Otherwise “a slight” overpressure.

p3090 I17 “The Teflon/glas chambers A, B and C were kept in pressure equilibrium with the laboratory, with the help of two open outlets as indicated in Fig.2. The mirror purge flow compensates for any leaking of the chamber.”

As well as description in the new section 3.2.5.

Referee 1: • Why did the authors use different chamber set up (Teflon and glass)? What are the consequences for the measurements if using one or the other set up?

Answer: We agree that this point should be clarified with the following text: “The glass chamber set up was the first set up which could be built easier than Teflon, but the cavity length is much shorter. In order to determine the path length it is useful to have different cavity lengths. Inserted at p3090 I17.

Referee 1: In the text, the author mention that set up B and C was used for ozone and nitrous acid, whereas also set up A is listed in Table 2. Please clarify.

Answer: Setups A, B and C were used for ozone and nitrous acid. Changed in the manuscript:

p3091 I7 “For the O₃ measurements the setups A, B, and C were used. For setup A both mirror sets, for setup B mirror set M2 and for setup C mirror set M1 were used (Table 2).”

p3091 I16 “For the nitrous acid (HONO) measurements setup A with both mirror sets, setup B with mirror set M2, and setup C with mirror set M1 were used (see Table 2),”

Referee 1: • Please add ozone and bromide monoxide concentrations in the chamber when describing the experiments.

Answer: We agree and provide the answers hereafter: Ozone concentrations were up to 2ppm. Inserted in manuscript at p3091 I11 “(up to 2 ppm).”

BrO concentrations were up to 1000ppt. Inserted in manuscript at p3092 I15 “A typical concentration up to 1000 ppt was measured.”

Referee 1: • p3093 I13-20 already describes one way, how the expected performance of the instrument was determined. I would suggest to move this part to the next subsection.

Answer: We do not agree with the Referee in this point. The determined absorption A is part of the mirror reflectivity and thus we think this part is in the right subsection. No change was made.

Referee 1: • In section 4.1 the determination of the mirror reflectivity and absorption in the mirrors is described. What is the accuracy of this determination? Looking at Fig. 3 it seems as if the absorption in the mirror becomes zero at wavelengths around 360nm to 370nm.

Answer: This is not unrealistic, as the absorption in this wavelength range is close to zero (on the given scale) and consistent with information from the manufacturer.

Referee 1: This is very unlikely at these wavelengths and indicates that the accuracy of the reflectivity measurements was limiting this determination. Please clarify and give numbers for the accuracy in the text.

Answer: We agree with the point of the accuracy and included it. The accuracy of the determination was inserted in Fig. 3. and at p3094 l11, p3095 l5, l11 and in the caption at table 5

Referee 1:• p3094 l6: I do not understand why the detection limit would be lower at lower concentrations of the absorber. If the absorber concentration is high the absorption features are best pronounced and large compared to other spectral structures whereas they are less pronounced at lower concentrations, so that other spectral features or noise in the instrument makes the determination of the absorber's spectrum less precise. As mentioned by the authors there are spectral structures, which are not constant over time, which would clearly make the determination of the absorption more difficult, if the magnitude of the absorption becomes smaller compared to the background structures. Please clarify.

Answer: This can easily be described and is in general applicable to broad band spectroscopy: "The relative error decreases with higher concentration. But at higher concentration larger residual structures arise due to imperfect description of the absorption bands. Thus the absolute error and detection limit increase." Inserted at p 3094 l7

Referee 1:• In section 2.4 experiments with more than one absorber are mentioned, but not described or discussed in the results.

Answer: At the BrO measurements, ozone and BrO were measured simultaneously. For a better understanding the plot of the fits in fig. 5 also shows the O₃ fit for the BrO measurement now.

Referee 1:• In the result section, the accuracy of measurements needs to be discussed. This would included a discussion of the accuracy and detection limit for a mixture of trace gases, when BrO concentrations are small compared to other absorbers like ozone.

Answer: We agree with the Referee and added the following text to the manuscript: "Example fits of different trace gases are shown in Figs. 5, 6, 7, and 8. The fit result in Fig. 5 shows an example where ozone and BrO were detected simultaneously, whereas only one absorber was present in the other examples (Figs. 6 – 8). Compared to the measurements where only single absorbers were evaluated, the first example (Fig. 5) shows an approximately 2 times larger residual. This is typical for DOAS measurements, however, detection and identification of the different absorbers is possible with sufficient sensitivity" Inserted at p3094 l8.

Referee 1:• Table 1: Why is the absorption length much smaller than the cavity length in setup A?

Answer: This can be answered by the glass chamber setup which was limited by the length of the available glass cylinder.

Referee 1: • Table 5: Please give the link between the path length in this table and the definitions in section 2.

Answer: We agree with the Referee and added the following text: “The path length L_{eff} (347 nm) is for setup B = 839m and for setup C = 1472 m” to the caption of table 5.

Referee 1: Why is there no detection limit for ozone in the set up with M_2 ?

Answer: Because there are only the best achieved detection limits given. For comparison of the mirror sets additional the BrO values of both mirror sets were shown.

Referee 1: Minor points:

- p3086 l23: a right parenthesis is missing Answer:corrected
- p3109 caption l2: “chambers” instead of “chamber” Answer:corrected
- p3094 l23: “values” instead of “figures” Answer:corrected
- Figure 1 and 2: I would suggest to increase the font size for the labels Answer:corrected

Additionally, we added the following corrections to the manuscript:

- p3082 l25 “m2” instead of “M2”
- p3086 l21 “3.1 Instrument” instead of “3.1 The instrument”
- p3087 l12 “3.1.1 LED Radiation Source” instead of “3.1.1 The LED Radiation Source”
- p3095 l2 “bands” instead of “band”
- p3095 l3 “over” instead of “of”
- p3095 l5-6 “,” instead of “for”, “with” instead of “of” and “T” instead of “transmission”
- p3095 l8 “wavelengths” instead of “wavelength”

Furthermore, the following improving expressions were added to the manuscript:

- inserted at p3082 l14: “measurements” instead of “tests”
- inserted at p3095 l19 after production process: “what is currently under development by different companies”
- inserted at p3095 l22: “For most measurements this is not applicable.”
- inserted at p3096 l2: “However this would also ease the compactness of the system.”
- Inserted at p3096 l17: “which are maybe even higher.”

Additional references:

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Plane, J.: Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, *Nature*, 453, 1232–1235, <http://dx.doi.org/10.1038/nature07035>, 2008.

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Buxmann, J.: 'Bromine and Chlorine Explosion' in a Simulated Atmosphere, Ph.D. thesis, Institute of Environmental Physics, University of Heidelberg, Germany, 2012.

Cantrell, C. A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, *Atmos. Chem. Phys.*, 8, 5477–5487, <http://dx.doi.org/doi:10.5194/acp-8-5477-2008>, 2008.

Additional References added to the manuscript, which were used in the answers for Referee #2 are listed in the Author comment for Referee #2.