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Atmospheric
Measurement
Techniques
Discussions

Interactive comment on "A Cavity-Enhanced Differential Optical Absorption Spectroscopy instrument for measurement of BrO, HCHO, HONO and O_3" *by* D. J. Hoch et al.

Anonymous Referee #1

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

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

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.

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

- 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?
- 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? 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.
- Please add ozone and bromide monoxide concentrations in the chamber when describing the experiments.
- p3093 l13-20 already describes one way, how the expected performance of the instrument was determined. I would suggest to move this part to the next subsection.
- 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. 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.

- 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.

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

- 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.

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

- Table 5: Please give the link between the path length in this table and the definitions in section 2. Why is there no detection limit for ozone in the set up with M2?

Minor points:

- p3086 l23: a right parenthesis is missing

- p3109 caption l2: “chambers” instead of “chamber”

- p3094 l23: “values” instead of “figures”
- Figure 1 and 2: I would suggest to increase the font size for the labels

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Interactive comment on Atmos. Meas. Tech. Discuss., 5, 3079, 2012.

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