Author comment on

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 #2

We would like to thank Referee 2 for the thorough review and helpful comments. We agree with most of the points given by the reviewer. Many modifications were made and additional measurements were included. In the following we want to answer directly to the provided comments.

Referee 2: This paper presents an in situ instrument to measure BrO, HONO, HCHO, O_3, and O4 in the 325 - 365 nm range. The light source is a UV-LED. The instrument is tested by introducing unknown concentrations of each of the target gases, and fitting the resulting spectra. The novel aspect of this paper is the use of a UV LED. This paper gives initial laboratory measurements. The measurement of BrO using broadband cavity enhanced spectroscopy with a Xe arc lamp in the same wavelength region has been reported previously (Chen and Venables, 2011).

Answer: We thank the referee for this nice summary.

Referee 2: Major comments:
- In situ measurement techniques can be tested by introducing known concentrations of analytes or by comparison with existing instruments. This is a major advantage of in situ instruments, compared to remote sensing techniques like DOAS. However, the authors have not performed any quantitative tests of their instrument.
Introducing unknown concentrations of each analyte shows the instantaneous precision of the instrument for single species, but it does not demonstrate accuracy or stability. Possible errors for this instrument include (but aren't limited to): loss of analyte in the inlet or cell; creation of HONO in the inlet or cell; drift in alignment of the mirrors; uncertainty in the dilution by the mirror purge volumes; uncertainty in the geometrical correction for the length occupied by the mirror purge volumes; uncertainty in the determination of the mirror reflectivity. It is relatively straightforward to produce known concentrations of O_3, HCHO, and HONO. Alternatively, it is possible to compare this instrument with existing instruments that measure these species. These tests should be completed.

Answer: We agree with the Referee and inserted a comprehensive comparison of our CE-DOAS system with a White-System DOAS and an Ozone Monitor (see also answer to Referee #1).
We do not agree to the comments concerning measurement errors. In comparison to other in-situ instruments, the presented CE-DOAS instrument features an open path measurement cell and thus can measure without inlet losses or wall losses. For clarification we included the following extensions:

Inserted at p3080 l9 start after instrument: "with an open path measurement cell"
Inserted at p3081 l12 start after essential: "without the risk of inlet and wall losses"
Inserted at p3081 l13 "CE-DOAS" instead of "cavity based measurement"

Inserted at p3081 l21 start after inlet filters: “and thus have the risk of losses on the inlet and filter, as well as possible chemical reactions”

The cells were only applied for proving the performance of the instrument. Dilution due to the purge flow is taken into account if appropriate. A newly included intercomparison shows that the derived errors are taken realistically into account.

Referee 2:- The authors do not test mixtures of the analytes. In the atmosphere, multiple absorbers will be present. Even in laboratory and chamber studies, it is likely that multiple absorbers will simultaneously be present. The authors do not demonstrate detection limits in the presence of multiple absorbers.

Answer: We could clarify this point, as we did test different mixtures. While performing BrO measurements, O_3 and BrO were measured simultaneously. In order to make this procedure easier to understand the plot of the fits (fig 5) now show the O_3 fit at the BrO measurement.

Referee 2:- NO_2 also absorbs strongly in this spectral region, but it is not mentioned in this paper. At 345 nm, the NO_2 cross section is approximately 4 x 10^{-19} cm^2. For 10 ppb of NO_2 at sea level, this is an extinction term of $9e^{-8}$ cm^{-1}. This is a large optical extinction relative to the other absorbers. What detection limit do the authors achieve when they introduce a mixture with atmospherically-relevant concentrations of NO_2? What detection limit is possible with the higher concentrations of NO_2 that might be used during lab or chamber experiments?

Answer: We like to thank the reviewer for this remark. Indeed NO_2 detection would have been possible, but were not the focus of this work, as the UV-wavelength range is not optimal for NO^2 detection. Nevertheless an estimate of the detection limit can be made. As mentioned, the NO_2 cross section is approximately 4 x 10^{-19} cm^2 at 345 nm. The residual structures of the CE-DOAS have a typical peak to peak value of 3 x 10^{-3}. A maximum light path of 816 m leads to a detection limit of 3.6 ppb, which would be sufficient to detect NO_2 in a moderately polluted environment.

Change to the manuscript: The above value was inserted in table 5.

Referee 2:- The analysis approach and equations have been previously presented by Platt (2009) and do not need to be repeated here.

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

Referee 2:- Does the spectrum of the LED change while it is being pulsed?

Answer: Extensive noise characterizations of the LED showed that the LED spectrum did not change while the LED was pulsed.
Inserted at p3087 l19 start after continuous operation: “, while the spectrum of the LED does not change.”

Referee 2: Other comments:
- The time for the cavity to reach optical equilibrium is approximately 3.7 μs, calculated for mirrors of reflectivity 0.9991 and 1 m cavity length. This is small relative to the 750 μs that the LED is powered on, but this issue should be discussed.

Answer: We agree with the Referee and included the following clarifications:
"The time for the cavity to reach optical equilibrium is approximately 3.7 µs, calculated for mirrors of reflectivity 0.9991 and 1 m cavity length, leading to a maximum light path of (1/(1-0.9991))m. This is small compared to the 750 µs that the LED needs to reach full intensity when powered on." Inserted at p387 l21

Referee 2:- What is the integration time of the CCD in these measurements?

Answer: Please see at p3090 l28: "A spectrum with 85% of full saturation could be obtained in 9.50 s with mirror set M1 and 3.50 s with mirror set M2. Based on noise tests, 30 spectral scans were taken and co-added for mirror set M1 and 50 spectral scans were taken and co-added for mirror set M2 to achieve sufficient measurement accuracy. This corresponds to a temporal resolution of 4.8 min for M1 and 2.9 min for M2."

Referee 2:- Why doesn't the detection limit scale as the square-root of the measurement time?

Answer: Please see at p3095 l12: "The reason is that the detection limit of a DOAS-measurement is not only dependent on the photon noise, but also on spectral structures which are not constant in time. Other sources for increasing noise are electronic noise and optical noise like the LED light source, optical fibers and spatial inhomogeneity of the optical grating of the spectrograph."

Referee 2:- Where is the pressure measured? Using O4 to calculate the cavity loss (or pathlength) will require accurate knowledge of the pressure.

Answer: We agree with the Referee and inserted at p 3092 l6: "next to the chamber (the same values assumed as in the chamber)"

Referee 2:- What is the measured optical power output of the LED? How does this compare to a Xe arc lamp, and is the LED a better light source?

Answer: Both questions are considered important by us and are answered in detail below. The changes made to the manuscript are further listed below. The first question on the optical output power is answered by the S-ET data-sheet, which provides a value of 400 µW. This quantity needs to be compared to a xenon arc lamp. The question if the LED is "a better light source", however, may not ultimately be answered here because the choice of light source depends on the application. Therefore, we would like to add the reasoning which led to the choice of using an LED in this proof-of-concept study.
When comparing the output power of an LED to that a xenon arc lamp, one needs to consider the radiance depending on the respective wavelength interval used for the spectroscopic measurement. The luminescent wavelength range of LEDs is relatively narrow while the emission spectrum of arc lamps may be approximated by that of a Planckian gray-body. In the following, we compare the spectral characteristics of the S-ET UVTOP340 to an OSRAM XBO75 W/2 Xe arc-lamp. The calculations are solely based on the figures given in the data-sheets.
We calculate the output power of both light-sources which may be coupled into the resonator, i.e. the radiance, for the applied evaluation range between 325 and 365 nm. Here, the XBO and the UVTOP have a radiance of 1.9x10^6 W m^-2 sr^-1 and 4.2x10^3 W m^-2 sr^-1, respectively. Thus, the arc-lamp has a radiance in this wavelength interval which is about 450 times higher compared to the LED. However, the optical output power in the 325nm to 365nm range per electrical input power for both devices is almost equal since the UV-LED consumes only 180 mW.

The authors, nevertheless, believe that applying LEDs is advantageous in this kind of cavity enhanced measurements, because

- The narrow emission spectrum of LEDs leads to much less stray-light in both the cavity and the spectrometer compared to arc lamps. As demonstrated in the paper, the wavelength range of high-reflectivity is relatively narrow compared to a Planckian emission spectrum. As a result, less filters are required and the instrument setup is less complex. This is especially important for cavity based instruments, since the light is coupled into the multireflection system through the highly reflective mirrors, thus light outside of the reflectivity curve is transmitted directly into the receiving fibre. This requirement differs from the White system typically operated with a xenon arc lamp, which is also used as a reference instrument in the new manuscript (see above). In case of a White system, the multireflection system might act as a filter itself if dielectric coated mirrors with a limited reflectivity range are used. Hence, the influences by instrumental stray-light induced by the broad band light source are significantly lower.
- In the present manuscript, a method to monitor the path length stability between measurements is described. This method requires a light modulation faster than the ring-down time of the cavity. While this is fairly easy to achieve for semiconductors, this is much more complicated if not impossible for continuously emitting arc lamps.
- The lifetime of LEDs is typically longer than for arc lamps. In the comparison between the UVTOP340 and XBO 75W/2, the lifetime of 3000h of the LED is considerably longer than the 400h of the xenon arc lamp. This improves the operability because the light source requires less adjustments. Additionally, the costs of operation are lowered.
- LEDs are much easier to handle than arc lamps and do not require a special housing. The power consumption is by far lower, as mentioned above, and less excess heat is produced. This is particularly useful in temperature controlled environments (e.g. smog chambers).
- Furthermore, UV-LEDs have the potential to become even more competitive as the semi-conductor technology evolves.

Parts of the aforementioned motivation to use LEDs are now included in the manuscript:

1) Inserted into the introduction (start after "... a UV-LED." in line 11 on page 3082; the following sentence starting "To estimate …" is shifted to an additional paragraph)

“Compared to the xenon arc lamp applied as light sources in previous experiments, UV-LED offer several advantages particularly important for cavity enhanced measurements: (1) The relatively narrow emission spectrum of LEDs reduces the amount of straylight within the instrument, because there is no light emitted outside the mirror reflectivity curve. Hence, less filters are required and the instrument setup becomes less complex. (2) The light output of LEDs may be easily modulated. It is thus possible with the instrument presented here, to monitor the effective path length by measuring the ring-down time between measurements. (3) The lifetime of LEDs is typically longer than for arc lamps. This feature improves the operability because the light source requires lesser adjustments. Additionally, the costs of operation are lowered. (4) LEDs are much easier to handle than arc lamps and do not require a special housing. The power consumption is by far lower, as mentioned above, and less excess heat is produced. This is particularly useful when the light-source is applied in temperature controlled environments like smog chambers.”

2) Inserted into the instrument description (add a second paragraph below 3.1.1 after line 21 on page 3087)

“The UVTOP340 delivers 400 µW of optical output power (SET, 2010). This figure is now compared to the optical output power of a 75 W xenon arc lamp as described by Kern et al. (2006). The quantity needed to compare the optical output of different light sources is the spectral radiance integrated in the wavelength interval used to evaluate for the trace gas absorption features called radiance. On the one hand, the radiance of the UVTOP340 between 325 and 365 nm calculates to 4.2x10^3 W m^-2 sr^-1 assuming a Lambertian emission pattern, an emitter area of 0.045 mm^2 as derived from microscopic measurements and a Gaussian emission spectrum (340 nm peak, 15 nm FWHM). On the other hand, the emission spectrum of a sample xenon arc lamp (XBO 75W/2 xenon arc lamp manufactured by OSRAM) is approximated by that of a Planckian gray-body with an emissivity of 0.17 derived from the photometric properties given in OSRAM (2012). The radiance of the xenon arc lamp between 325 and 365nm calculates to 1.9x10^6 W m^-2 sr^-1. Thus, the arc lamp has a radiance in this wavelength interval which is about 450 times higher compared to the UVTOP340. However, the optical output power in the 325 nm to 365 nm range per electrical input power for both devices is almost equal since the UVTOP340 consumes only 180 mW."

3) Inserted into the conclusions (add to the paragraph ending in line 27 on page 3095)

"While this work demonstrates that CE-DOAS measurements are feasible applying UV-LEDs as a light source, it needs to be noted that xenon arc lamps may provide a 450 times higher input radiance. When compared to the electrical input, however, both devices deliver a similar radiance per input power. Therefore, UV-LEDs may present a competitive alternative light source to xenon arc lamps depending on the application of the presented instrument. UV-LEDs have furthermore the potential to become even more energy efficient with the technological progress projected for the next years."

Additional references:
OSRAM: XBO 75W/2 Product datasheet, available at: http://www.osram.com (last access: 7 July 2012), 2012.

Kern, C., Trick, S., Rippel, B. and Platt U.: Applicability of light-emitting diodes as light sources for active DOAS measurements, Appl. Opt., 45, 2077–2088, 2006.

Referee 2:- What is the volume and size of the chamber?

Answer:
Setup A is a glass cylinder with a radius of about 5cm:
Volume setup A = 7.5 l
Setup B and C are Teflon cylinders with a radius of about 10cm:
Volume setup B = 40 l
Volume setup C = 50 l

This information has been added to table 1 in the revised manuscript.

Referee 2:- What literature cross sections were used in the spectral analysis?

Answer: Please see at p3105 table 3.

In addition to the above, we added some minor changes to the manuscript which are listed in the answer for Referee #1.