

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 #2

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This paper presents an in situ instrument to measure BrO, HONO, HCHO, O₃, 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).

Major comments: - In situ measurement techniques can be tested by introducing

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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 O₃, HCHO, and HONO. Alternatively, it is possible to compare this instrument with existing instruments that measure these species. These tests should be completed.

- 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.

- NO₂ also absorbs strongly in this spectral region, but it is not mentioned in this paper. At 345 nm, the NO₂ cross section is approximately $4 \times 10^{-19} \text{ cm}^2$. For 10 ppb of NO₂ at sea level, this is an extinction term of $9 \times 10^{-8} \text{ cm}^{-1}$. 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 NO₂? What detection limit is possible with the higher concentrations of NO₂ that might be used during lab or chamber experiments?

- The analysis approach and equations have been previously presented in Platt 2009, and do not need to be repeated here.

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

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Other comments:

- The time for the cavity to reach optical equilibrium is approximately 3.7 us, calculated for mirrors of reflectivity 0.9991 and 1 m cavity length. This is small relative to the 750 us that the LED is powered on, but this issue should be discussed.
- What is the integration time of the CCD in these measurements?
- Why doesn't the detection limit scale as the square-root of the measurement time?
- Where is the pressure measured? Using O4 to calculate the cavity loss (or path-length) will require accurate knowledge of the pressure.
- What is the measured optical power output of the LED? How does this compare to a Xenon arc lamp, and is the LED a better light source?
- What is the volume and size of the chamber?
- What literature cross sections were used in the spectral analysis?

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

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