



Interactive comment on “Inherent calibration of a novel LED-CE-DOAS instrument to measure iodine oxide, glyoxal, methyl glyoxal, nitrogen dioxide, water vapour and aerosol extinction in open cavity mode” by R. Thalman and R. Volkamer

Anonymous Referee #1

Received and published: 2 August 2010

This paper was an interesting read and the results of this study are certainly of interest to the atmospheric chemistry community. I recommend that this work be accepted after the following points have been addressed.

(1) The claim is made in the title and repeated several times over within the manuscript (e.g., lines 487–493) that this work constitutes a well calibrated measurement technique. However, this claim is not substantiated convincingly within the paper, at least

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not for the trace gases. While I would like to believe that the authors' measurements and data treatment are accurate, what is missing from this manuscript is a comparison with independent validated measurements of NO₂, glyoxal and/or methyl glyoxal abundances. For example, there are concentrations given on lines 489 and 490 and in Figures 8 and 9. How did the authors verify that these numbers are indeed correct, given that there was so much drift in the mixing ratios? Just as was done for the aerosol, it should have been possible (and easy) to generate a calibrated gas stream containing NO₂, for example.

(2) The authors use both an open and closed cavity, and state that they made “the first well-calibrated CEAS measurements in open air.” It would therefore have been nice to see a discussion why the use of an open cavity would be preferred. Sure, there are obvious advantages because there are no inlet losses. However, not all surfaces are eliminated. There is, for example, the optical table, where gases could absorb to or evaporate from. Also, it seems to me that lower detection limits are achievable when aerosols are removed (e.g., via a filter) – see Table 3. Another potential problem with the open cavity design is that the purge gas could slowly fill the space between the mirrors when there is little air movement. Thus, it's not at all obvious why the open cavity would be advantageous.

(3) The various “first” and “novelty” claims were distracting from the otherwise good work and sometimes unjustified. For example, cavity-enhanced absorption spectroscopy with light emitting diodes has already been demonstrated by several groups, and “calibration” of optical path length using O₄ is hardly new in the DOAS community.

Specific points:

line 31. 30 - 70 Mm⁻¹ seems like a narrow range for aerosol extinction values. Is there a reason for this?

line 50: As far as I know, the cells are known as Herriott-type, not Harriet-type. While both are widely used, they have been surpassed by astigmatic type cells (e.g., J. B.

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McManus, P. L. Kebabian, W. S. Zahniser, Appl. Optics (1995) 34, 3336). It would also be good to simply state the path lengths that can be achieved with the various types of cells rather than giving the difference as a factor.

lines 54-66. This sentence is awkward to read (mainly because of the way papers are cited in ACPD). Consider consolidating the references in the form of a table, or add to Table 1.

lines 76-78 “This potential had as of yet not been developed.” It sounds like this would be as simple as placing a (Teflon) filter on the inlet. This has really not been tried with CE-DOAS? I’d have thought someone would have done this by now.

lines 149 - 140 – The reference Volkamer et al 2010 was incomplete; hence, I am not sure how IO and glyoxal are relevant to climate – are they?

line 150 “the first well calibrated CEAS measurement” – were other CEAS instruments used that were not well calibrated (e.g., Washenfelder et al.)? Or are these the first measurements of a well-calibrated instrument? Consider rephrasing as to avoid the confusion.

line 154. Consider rephrasing the sentence as Figure 2 also shows a DMA and aerosol generation equipment. For a fraction of a second I wondered if a DMA was needed to run a LED-CE-DOAS....

line 160, line 173. Please state what constitutes a “good” match of LED and mirror reflectivity (wavelength? output power? beam size?)

line 184 reflectivity of 99.996% - is this measured or stated by the manufacturer? At what wavelength?

line 354-356. “We can account for the distortion in L by applying a correction factor $F(\lambda)$ to $\sigma(\lambda)$.” This is perhaps the most interesting aspect of this paper. Couple of questions: 1) If the distortion is really in L, why not scale L instead of the cross-section (eqn 6)? 2) What values does F typically take? Since this method is applied in Figure 5, consider

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showing F as a function of wavelength in 5B.

lines 365-377. The ratio of $ds/d\lambda$ can, potentially, vary for different trace gases, and may be shorter for IO than for NO₂. Please comment on the analytical uncertainty that this may introduce.

line 455. Please define PSL.

line 478. Subscript missing for NO₂.

line 488. Strike the word “room”. “between the mirrors” already defines the space and is more accurate.

lines 496 – 497. “the first CE-DOAS detection of glyoxal and iodine oxide are accomplished.” Didn’t Washenfelder et al detect glyoxal using cavity-enhanced differential optical absorption?

line 498. “The innovative use...” The use of diodes in CEAS is not new – see Ball et al., CPL (2004) 398, 68-74, and Kasyutich et al. Appl Phys B (2003) 76, 691-97 – so it’s not clear to me what was innovative here. Consider striking the word “innovative”.

Lines 492-531. The conclusion section is somewhat unusual in length and contains a lot of things that better belong in a discussion section. For example, lines 502-504: While LEDs are likely longer-lived and have an unstructured and constant in time emission spectrum, these are not conclusions of this study but rather discussion points. Consider reorganizing this part of the manuscript.

Table 1 – it would be informative here to have a column with detection limits and integration time.

Table 3 – define detection limit (3 sigma, 2 sigma) as a courtesy to the reader – I know it’s stated on line 408-409 but it took me 1 hour to find it there.

Figures – general comments. It was sometimes not clear what was plotted and why, and too many traces were on the same graph (e.g., Fig. 1, Fig 7b, Fig 3 etc) making

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the Figures unnecessarily confusing. Furthermore, the fonts and sizing of labels were inconsistent from Figure to Figure.

Figure 1 – I am not sure I fully understand this Figure as the caption is inconsistent with the graph. The caption says that are 2 scenarios plotted: free tropospheric conditions ($\text{AOD} = 1 \times 10^{-7} \text{ cm}^{-1}$ at 450 nm, thin dashed line); and polluted urban conditions ($2.5 \times 10^{-6} \text{ cm}^{-1}$ at 450 nm, thick dashed line). The thick dashed line appears at 10^{-3} cm^{-1} , while the thin line appears at 10^{-5} cm^{-1} . The latter two seem a bit high. Also, it would have been helpful if all quantities were explained. What is “mirror loss” and how was it determined? What was the equation used to calculate the path length? What Rayleigh scattering cross-sections were used etc.

Figure 3 – caption is missing on the bottom axis

Figure 4 – As this Figure has been published elsewhere, I recommend simply citing the earlier work rather than republishing the same information. Also, I am not sure why the dashed line for the Acton/Pixis would fall so far below the experimental points?

Figure 5 – caption is missing on the x-axes. What are the uncertainties in the mixing ratios? It is stated that the cross-section is “scaled” by $F(\lambda)$. By how much? Since the scaling was wave length dependent, please add a panel showing the scaling factor as a function of wave length. Could the scaling factor be expressed as a function of the mirror reflectivity?

Figure 6 – Panel A. Consider changing the word “average” to “effective” as “average” implies an arithmetic mean (which I am not sure is correct here).

Figure 7 – Panel A, vertical axes are missing titles and units. SCD is missing units. Panel B – I am not sure what the authors are trying to show in this Figure. Is it connected in any way to Panel A? How was the O4 path length varied? Also, I am not sure of the detection limits for IO: At 12:25 pm, it is somewhere between 1 and 2 ppb, but -5 ppb are measured. Shouldn't the detection limit be at least as high as the offset

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uncertainty?

Figure 8 – Panels B and C. Please label the extinction values with a subscript of their wavelength. Panel D. I assume that the main point of this Figure is in the fact that at 12:20 pm, when the aerosol is removed, the NO₂ number density deduced remained constant, whereas the Slant column density changed. Please also add a panel showing the changes in [O₄].

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 2681, 2010.

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