

Interactive comment on “Measurement of glyoxal using an incoherent broadband cavity enhanced absorption spectrometer” by R. A. Washenfelder et al.

Anonymous Referee #2

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General Comments

This manuscript describes an instrument which represents not only a potential breakthrough in the spectroscopic measurement of glyoxal, an atmospheric species that is notoriously difficult to measure accurately, but in the use of Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS) as a means of detecting ambient species. The reported precision for NO₂, 20 parts per trillion in 1 minute integration time, is within range of that reported for a non-dispersive cavity enhanced monitor employing an incoherent light source, ~20 ppt in 10 seconds[1] and its performance surpasses to my knowledge, that of any reported conventional CRDS system.

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I note that Referee #4, who must be an expert in IBBCEAS, has provided a rather thorough and insightful review with which I heartily concur. I therefore ask the following general questions as a person who works in a related area, but is not totally familiar with all the intricacies of IBBCEAS and wishes to understand its strengths and weaknesses.

1. Why is this instrument better than those that have come before it?

My perusal of the literature indicates that the reported performance of this instrument is a factor of five better than any previously reported NO₂ measurement using a IBBCEAS instrument.[2] Is this primarily due to improvements in experimental technique (brighter, more stable light source; lower noise detector; better mirrors, etc.) or because of the retrieval routine? If it is the latter, is the assumption that there are no unknown spectrally structured absorbers a good one outside of the laboratory? (I will address this issue later.)

2. How is the precision determined and what is the instrument drift?

This question echoes many of the comments made by Reviewer #4. The authors have provided no roadmap as to how the instrument is actually operated. To obtain a concentration reading, the mirror reflectivities and reference spectrum must be predetermined. How often is this done? The fluctuations in total lamp intensity are removed by measuring the overall lamp intensity, but is the spectral output really that constant? Is the reported precision just the standard deviation of a small number of measurements obtained over a relatively short time span? In addition, an Allan plot[3,4] of baseline drift would be useful to the casual reader in order to provide an indication of the stability of the instrument, an important consideration.

3. What is the actual sensitivity for glyoxal at typical concentrations in an NO₂ background?

Perhaps more importantly, the stated precision for glyoxal is for relatively high amounts of that species in dry air. While that is sufficient for a laboratory measurement of

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glyoxal, it begs the question of how good the precision and drift are when attempting to extract 0-300 ppt concentrations of glyoxal in a background of 10-30 ppb of NO₂. The data in Figure 7 is presented as providing an answer to this question. However, it fails to do so. The correlation plots in panels b and c are beside the point; similar plots have already been provided. In fact, the CRDS glyoxal measurement is sufficiently prone to noise and/or drift that it provides little information. What should be presented is a plot of the actual IBBCEAS data on an expanded scale which would provide a closeup of the effect of turning the NO₂ on and off on the measured glyoxal concentrations. Peering at a highly expanded version of Panel a on my computer screen, it appears that the presence of NO₂ does cause a small, but significant (i.e., on the order of 100 ppt) drop in the measured glyoxal, an effect which could just be an artifact of the figure/file creation or represent a real problem. (See the next paragraph.) I also have questions as to why the NO₂ concentration shows the large amount of drift that it does in both instruments for the high concentration case and why the CRDS measurement is still drifting upwards in the low concentration case when the IBBCEAS measurement appears to be relatively flat?

Furthermore, in Figure 8, Panel b, the glyoxal data indeed shows a precision that is consistent with the reported number. However, the reported values are consistently below zero, a fact which is left unexplained. This trend continues for the data in Panel c, where the water vapor baselines are also consistently below zero. This would appear to be, again, a baseline subtraction issue.

If this issue is not truly settled, it should be mentioned in the abstract and in the conclusions section.

4. What are other real world limitations on the accuracy of the measurement?

Is the assumption that the presence of particles can be dealt with as assuming that they provide a varying change in the background similar to that of Rayleigh scattering justified? While this is true for small ($d < 400$ nm) particles of albedo=1, absorbing

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particles (e.g., black carbon) will tend to have a relatively flat spectral response and not mimic the Rayleigh scattering. Will this cause an offset? In addition, larger particles will show oscillatory scattering intensity as a function of wavelength. Are you just better off using a Teflon filter to remove particles and not dealing with this issue.

Is it possible that the presence of finite amounts of water vapor could cause problems? Both Keabian and co-workers[1] operating a LED at 440 nm and Hargrove and co-workers[5] using a laser at 405 nm have observed anomalous extinction in the presence of water vapor. Hargrove, et al. ascribed this effect to a heretofore unknown water absorption band, but Keabian et al. have suggested that the cause is water adsorption on the mirrors at sub-monolayer concentrations. If this water adsorption occurs in the present apparatus, won't it be rather difficult to correct for, as both reference spectra and mirror reflectivity measurements are made using dry gases?

Other Comments

1. In response to referee #4, for the spectral range used to detect NO₂ and glyoxal, the relevant O₄ band, which is centered at 446.7 nm, has a peak absorption coefficient of $\sim 10^{-9}$ cm⁻¹ given that air is only 20% oxygen. This should be barely detectable, although typical pressure fluctuations of 2-3% would not be.
2. I strongly agree with the comments of Referee #4 about the fact that the correlation plots of the CRDS with the IBBCEAS instrument deviate from 1 by identical amounts for both NO₂ and glyoxal strongly suggest that there might be a systematic error in retrieving the spectrum for both compounds.
3. Are the authors concerned with the issue of temperature control with respect to the issues of water vapor adsorption, mirror reflectivity, etc.? Would an elevated temperature help or hinder quantitative glyoxal transport through the system?
4. Subject to clarification of the points raised above, I suggest that the abstract be modified to include the fact that glyoxal and nitrogen dioxide have a complete spectral

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overlap. This would make it clear to the uninitiated reader as to the magnitude of the problem.

References

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