

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

R. A. Washenfelder et al.

Received and published: 22 November 2008

We thank the reviewer for useful comments on the manuscript. Listed below are our responses to the comments and the corresponding changes made to the revised manuscript.

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. 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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



spectrally structured absorbers a good one outside of the laboratory? (I will address this issue later.)

Many of our instrumental choices, including brightness of the light source and high reflectivity of the mirrors, may contribute to the quoted detection limit. However, we have not undertaken a side-by-side comparison with any other NO₂ IB-BCEAS instruments and it seems inappropriate to speculate on the comparison. Instead, we prefer to present a detailed description of our instrument with figures demonstrating the precision achieved.

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.

The reviewer makes an excellent point. We have added Section 2.4 to describe the operation of the IB-BCEAS. We believe that this will also address both reviewers' questions about pressure dependence.

In addition, we have clarified the statement of uncertainty in both cases.

Pp. 16530 lines 15 - 16: "The 1 σ standard deviation for 1-min IB-BCEAS measurements of 1.13 ppbv NO₂ is 20 pptv. *This represents the 1 σ range in retrieved NO₂ concentrations for a sequence of 1-min measurements with a sample of well-defined and constant composition.*"

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Pp. 16531 lines 13 - 15: "The 1σ standard deviation for 1-min IBBCEAS measurements of 4.5-ppbv glyoxal is 29 pptv. *This represents the 1σ range in retrieved glyoxal concentrations for a sequence of 1-min measurements with a sample of well-defined and constant composition.*"

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 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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



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.

We appreciate the reviewer's concern. Figure 7 demonstrates that the concentrations of CHOCHO and NO₂ can be retrieved simultaneously, and that a large concentration change in each has little effect on the retrieval of the other. Based on the reviewer's suggestion and the data in the figure, we have given quantitative limits for the potential effect of NO₂ on the accuracy of the CHOCOH retrieval:

Pp. 16532 Line 10: "[deleted: There is no evidence for interference in the retrieved concentrations of the two species in the IBBCEAS instrument.] *For the IBBCEAS instrument, the step changes of 15 ppbv and 7.5 ppbv NO₂ shown in Fig. 7a change the quantitative retrieval of CHOCHO by no more than 4.5%.*"

As the reviewer notes, the CRDS measurements shown in Figure 7 are of low quality due to instrumental difficulties with the diode laser. However, these measurements are still useful as an independent comparison.

The correlation plots shown in Figure 7b and 7c may seem to repeat the correlation plots shown in Figures 4 and 6. However, Figures 7b and 7c show that consistent retrievals are obtained for a mixture of strong absorbers. This is an important additional piece of information, and we do not feel that these correlation plots are "beside the point," as the reviewer suggests.

Regarding the baseline offset in Figure 8, we have added an additional statement:

Pp. 16535 Line 29: "*Subsequent work has shown that baseline drift during ambient measurements can be minimized by increasing the frequency of zero air and Helium reference measurements.*"

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Finally, we note that DOAS measurements have been used to simultaneously retrieve NO₂ and CHOCHO concentrations, and we have added the following statement:

Pp. 16532 Line 4: "*Published DOAS measurements, using spectra with similar resolution (~0.4 nm FWHM) and shorter pathlength (4.4 km) have been used to retrieve CHOCHO concentrations between 0.15 - 1.8 ppbv with NO₂ background concentrations up to 80 ppbv (Volkamer et al., 2005a).*"

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 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.

For a field instrument, aerosol can be eliminated by sampling through a filter, as described on pp. 16535 lines 10 - 17.

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?

We are aware of the discussion of anomalous water vapor extinction described

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



by Hargrove et al. (2006) and Kebabian et al. (2008). However, we observe no anomalous water vapor extinction for the IBBCEAS (at 441 - 469 nm) or CRDS (at 404 nm) instruments. Furthermore, the IBBCEAS instrument is designed with purge volumes adjacent to the mirrors that can be continuously flushed with a small flow of dry zero air, protecting the mirrors from contact with sampled air. Based on our experience with similar designs for cavity ring-down instruments, we do not anticipate problems with condensation on the mirrors.

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.

We thank the reviewer for this comment. Pressure fluctuations of 2 - 3% are quite large (20 - 30 hPa). We regularly acquired zero air spectra at similar pressure to the sample. Section 2.4 now describes the sequence of data acquisition and should resolve these questions about pressure dependence.

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.

Please see response to Reviewer 4.

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?

We have added a statement to address the issue of water vapor adsorption and mirror reflectivity:

Pp. 16521 line 20: "*Purge volumes may be used to maintain mirror cleanliness*

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

during atmospheric sampling, but were not used in these experiments, which were conducted primarily in particle-free zero air."

The laboratory measurements of glyoxal were conducted in dry zero air. The agreement between the IBBCEAS and CRDS instruments shown in Figure 6 indicates that sampling losses of glyoxal in the system are small. We have not yet conducted experiments to determine if elevated temperatures is useful for ambient measurements of glyoxal measurements at higher relative humidity.

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

We have added this statement in the introduction:

Pp. 16520 line 24 - 26: "IBBCEAS is an excellent detection method for atmospheric trace gases with broad, structured absorptions in the visible and ultraviolet spectral regions, and is particularly useful for simultaneously determining the concentration of molecules with significant spectral overlap, such as CHO-CHO and NO₂."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 16517, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

