Atmos. Meas. Tech. Discuss., 3, C1154–C1161, 2010
www.atmos-meas-tech-discuss.net/3/C1154/2010/

Atmospheric
Measurement
Techniques
Discussions

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 #2

Received and published: 13 August 2010

A couple of dozen research groups around the world have devised cavity-based spectrometers to quantify atmospherically important trace gases, tested their instruments under laboratory conditions and (in rather fewer cases) deployed them outside the laboratory to make field observations. A growing subset of these cavity spectrometers, like the instrument described in this paper, favour a broadband approach where the absorption spectrum of the atmospheric sample is recorded over a wide wavelength range in order to (i) identify the atmospheric absorbers by their unique absorption spectra, and

(ii) quantify several absorbers in the same wavelength window. The broadband (LED or arc lamp) approach is particularly suitable for measuring absorbers that possess broad, structured absorption bands at visible wavelengths, such as the atmospheric absorbers tested in this work. Thalman and Volkamer's paper will therefore be of interest to the many practitioners of cavity-based spectroscopies, as well as the wider atmospheric science community who wish use the results obtained by deploying such instruments in field work.

For me, the two principle advances of this work are (i) the first published detection of methyl glyoxal by cavity enhanced absorption spectroscopy and (ii) a novel analysis method wherein the authors apply DOAS methods to infer absorber concentrations and aerosol optical extinction from only the spectrum of light intensity transmitted through the cavity, I(λ), (i.e. without acquiring the cavity's background I_0(λ) spectrum in the absence of absorbers). The former adds another compound to the growing list of atmospherically important trace gases detectable by cavity methods, and the latter analysis approach is potentially useful when operating cavities in open path mode to avoid losses of reactive species to the cavity's internal surfaces (an approach first deployed for cavity work by Bitter et al, ACP, 2005). The use of water and oxygen dimer absorptions, which are ubiquitous and usually well-defined in ambient samples, to check the effective path length of the measurement is a clever idea (if not entirely new to this work): the bandwidths of most broadband cavity spectrometers will include H2O or O4 absorption features and, whilst these features will be a familiar sight to operators who use their instruments on ambient air, few groups employ the information carried by these absorption features to the extent that is being proposed here.

Otherwise, this study builds on a substantial body of broadband cavity work stretching back nearly 10 years, some of which is referenced by Thalman & Volkamer, some of which is unfortunately not. I agree with Anonymous Referee #1's comment (3) that the authors' over-used claims to be "first" and/or "novel" distract from an otherwise good paper and are sometime unjustified. I urge the authors to revise their manuscript to address the comments of Ref 1 and Gomez Martin. The authors might also note:

Aerosol extinction has previously been measured at 570-590nm by Thompson and Spangler using broadband integrated cavity output spectroscopy ICOS (Applied Optics, 2465, 45/11, 2006) and at red wavelengths by Varma et al using incoherent broadband CEAS (Applied Optics B159, 48/4, 2009). The latter is referenced by Thalman & Volkamer on p2685 in the context of using the O2 B-band at 690nm to calibrate mirror reflectivity, but they seem to have missed an obvious foretaste of the present work where Varma et al also discuss how the differential absorption of the O2 band was diminished by a reduction in intra-cavity effective path length caused by aerosol extinction. In the present blue wavelength region, Washenfelder et al also report a time series of aerosol extinction co-measured with their glyoxal detection (fig 8).

p2682 line 12 "...first CEAS detection of methyl glyoxal, and the first CE-DOAS detection of glyoxal and IO". Likewise p2701 line 12. As I said above, I believe the first statement is true. The second depends on nomenclature and whether one considers CE-DOAS to be its own separate spectroscopic technique. To me, CE-DOAS, BBCEAS, IBBCEAS and BB-ICOS are all variations on a common theme – certainly the apparatus/hardware is pretty similar, and the measureable produced by all these is an absorption/extinction spectrum of the sample over an extended bandwidth. Therefore I'm sceptical whether it is justifiable to claim glyoxal and IO as firsts for CE-DOAS when (as the authors acknowledge later in the introduction) these have previously been detected by other groups using other closely-related BB methods. Gomez Martin's comment about the paper's title is helpful here too: perhaps the adjective first [novel] should apply to the spectral analysis [calibration method], and not to the technique.

p2684 "CEAS measurements to date require separate calibration measurements to characterize the temporal variability of aerosol extinction..." and "CE-DOAS holds the promise to decouple aerosol and trace gas extinctions...". Again, this is not a unique feature of CE-DOAS and/or the present work. The sample's extinction coefficient measured by BBEAS (and related BB cavity methods) is commonly decomposed into a

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

sum of structured molecular absorptions and unstructured continuum absorptions due to Rayleigh and Mie scattering via equations analogous to the present work's Eqn 4. The various molecular contributions are then separated from the broadband continuum by multivariate fitting of differential absorption cross sections (Langridge et al, Analyst, 2006; Washenfelder et al 2008; Varma et al, 2009 and many others). Spectral fitting process has been discussed in detail in two reviews of broadband cavity methods which the authors don't reference (Ball & Jones, Chem Rev, 2003; Ball & Jones, "Broadband Cavity Ring-Down Spectroscopy", in Cavity Ring-down Spectroscopy: Techniques & Applications, ed G Berden & R Engeln, Blackwell Publishing, 2009). Thus existing methods *are* capable of quantifying aerosol extinction. I suspect the reason why aerosol extinction isn't commonly reported in the literature is because it's not straightforward to know how to partition the continuum absorption (after subtraction of Rayleigh scattering) between aerosol extinction and the effects of instrument instability. Reductions in the cavity throughput due to degradation of the mirror reflectivity, the cavity becoming slightly misaligned, small changes in the light source intensity (cf p2687 line 17), atmospheric turbulence (cf p2693 line 13) etc... can all give rise to an apparent continuum absorption signal that, usually being unstructured too, is very difficult to separate from the aerosol extinction. Unless I've missed something, I'm not sure that the authors' novel DOAS analysis method (and the assertion in line 15-17 of p 2693) provides a solution to this problem: everything still seems to be aggregated into the "polynomial" in Eqn 5. The difficulty of separating unstructured contributions to access just the aerosol extinction is illustrated in Section 3.6 measurement of IO, where the authors have to assume that all their broadband extinction is due to I2 (whose spectrum is unstructured at blue wavelengths) and that "no aerosol was present". [One caveat: iodine oxides nucleate new aerosol particles in the atmosphere – e.g. McFiggans ACP 10, 2975, 2010 and references therein]. Are there any non-aerosol broadband contributions to Eqn 8 on p2698?

p2687 line 4 "...the first well calibrated CEAS measurements [A] of trace gases [B] and aerosol extinction [C] by a single measurement [D] in open cavity mode [E] under atmospheric conditions [F]". Likewise p2701 lines 6 and 8. I hope the authors don't mean to suggest that other CEAS measurements were poorly calibrated. Consider rephrasing. Anyway, the combination of A+B+C+D+E+F has been achieved by Andy Ruth's group and others.

p2687 line 14 "LED well matched to the mirror reflectivity". p2693 line 5 "use the mirror reflectivity to balance the light intensity across the detector". This consideration isn't novel: the first demonstration of BBCEAS with LEDs (Ball et al 2004) noted the need to match the LED output spectrum to the mirror reflectivity. Ball & Jones (2009) discuss this in detail: their Fig 3.8 illustrates the same effects as the current Fig 3.

p2687 line 25. It'd be interesting to see a plot of the LED output as a function of time and some quantitative discussion about the long-term stability of the LED output (especially given how instrument instability can lead to continuum absorption signals that potentially compromise aerosol extinction measurements).

p2688 line 3 "optimum emission pattern" – do the authors mean "emission spectrum", or is there spatial inhomogeneity across the emitter's surface?

p2689-90 Nice comparison of the performances of the two spectrometers. But I was left unsure about how much of the Acton system's better performance was due to it being an intrinsically more advanced grating spectrometer versus how much was due to its multi-core fibre distributing the cavity output light vertically onto its entrance slit. The 1mm dia fibre into the OceanOptic's 100 micron slit will necessarily lose a majority of the intensity.

p2691-92 – see also comment 2 by Ref #1. I recognise there are applications where there's an advantage to run the cavity open-path. However, even with the present CE-DOAS analysis approach, it's still necessary to first characterise the mirror's reflectivity carefully as a function of wavelength using (in this case) He and N2 Rayleigh scattering; similarly for determining the fraction of the path occupied by the mirror purge gas. To do this, the present instrument has been constructed to allow a tube to be placed

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

between the mirrors to exclude ambient air. Given that I0(λ) spectra are still acquired for characterisations, I'm still unclear about the over-riding benefits of running ambient air measurements based solely on I(λ) compared the usual approach of having both I(λ) and background I0(λ) spectra with which to calculate the ambient sample's absorption. The latter can still be performed open-path, with the cavity tube being replaced periodically to acquire I0(λ) spectra. Monitoring the H2O and O4 bands would inform when new I0(λ) spectra are needed.

p2693 line 7 et seq: a measurement bandwidth of 70 nm "... about 2-3 times wider than previous CEAS instruments". LED-BBCEAS measurements of NO2 by Hollingsworth & Ball over a 420-485nm bandwidth are discussed in Ball & Jones 2009. This text book (literally!) example needs to be included in Table 1. Ball & Jones also discuss (i) the merits of performing measurements over as wide a bandwidth as possible (this is a general axiom in long-path and max-DOAS community), and (ii) restricting the DOAS fitting window to exclude particularly noisy data at the wavelength extremes of BB spectra (see also Gomez Martin's comment about the reduced information content of the IO spectrum at long wavelengths, p2697).

Section 3.2: I wonder whether slant column density is the best quantity to use here. Sure, it's very useful in long-path and passive DOAS where the concentration of absorbers vary along the light path. But (excepting the mirror purge regions) atmospheric samples ought to be homogeneous over the length scale of the cavity. SCD, optical depth and absorption/extinction co-efficient (cm-1) are all variously used in the figures, making the reader work hard to process their content.

p2695: Why have the authors chosen weight the molecular absorption cross sections by F(λ), rather than the more usual convention in BBCEAS of using the cavity enhancement factor 1/(1-R) to adjust the measured absorption spectrum for the wavelength dependent effective path length? The presence of residual structure around 440nm in the uncorrected Fig 5a is unsurprising, because here the cavity mirror reflectivity drops off quickly.

Sections 3.7 and 3.8. The O4 and H2O bands provide information on the aerosol extinction at 477 and 443nm, but how is this enough to infer what happens at other wavelengths (to “interpolate the wavelength dependence of the aerosol extinction for the NO2 experiment” p2700 line 10)? Have I misunderstood: surely the λˆ(-3.8) wavelength dependence of the aerosol extinction can’t be retrieved from just two wavelengths? I agree that one can infer much more about the wavelength dependence of the aerosol extinction if there’s a structured absorber like NO2 spanning the full measurement bandwidth. But as Gomez Martin comments, one can’t rely on such helpful absorbers necessarily being present in ambient samples. Also ambient aerosol is obviously more complex than the mono-disperse aerosol used in the current tests: what can one learn about ambient aerosol from two relatively closely spaced extinction measurements? (see also comments by Ref #1).

p2701 line 4 and Fig 10: are the quoted methyl glyoxal and glyoxal concentrations representative of ambient air in the authors’ lab? [They’re reasonably similar to concentrations in Fig 5 where the dicarbonyls were produced by evaporation from liquid solutions].

The Conclusions section in particular needs significant work to incorporate the comments above, analogous comments of the other referees, and to place the present study more modestly in the context of previous work.

Figure 3: why does the mirror reflectivity appear to increase (noisily) at short wavelengths <410nm?

Figure 7: Please indicate e.g. when the I2 photolysis & O3 generating lamps were turned on/off. Is this what causes the structure in the I2, IO and O3 time series? Panel A needs y-axis labels.

TECHNICAL CORRECTIONS:

p2688: two 2.5 cm diameter mirrors;

2 inch f/1 lens.... 1 inch f/4 lens – inch measurements are diameters or focal lengths?

p2690: N = sqrt(N)/N ....is N trying to convey two different quantities here?

p2690: define lpm, sccm

p 2698 line 12: For measurements in the ambient atmosphere, aerosols are likely to contribute...

Section 3.8: polystyrene latex spheres = PLS

Figure 6a: should the line be green for N2 in the legend? Is it possible to put error bars on the black and red data points in panels b & c to help judge whether the retrieval error has plateaued at 4th and 5th order polynomial?

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