

Interactive comment on “Using a high finesse optical resonator to provide a long light path for differential optical absorption spectroscopy: CE-DOAS” by J. Meinen et al.

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Meinen *et al.* have developed and demonstrated a robust, portable, and sensitive spectrometer for *in situ* and open path measurements of the NO₃ radical; a recent NO₃ intercomparison campaign has served to validate both their instrument and a system we deployed based on the same principle (Varma *et al.*, 2008). A central focus of their paper concerns the quantification of absorbing species and the description of the “optical path” or “pathlength” in the cavity. However, three considerations make the concept of pathlength problematic when applied to broadband systems. Firstly, different photons spend different times in an optical cavity and therefore travel differ-

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ing distances through the sample. This can be illustrated by referring to Fig. 2 of the Meinen paper: the intensity at time $10 \mu\text{s}$ (for instance) arises from photons that spent $10 \mu\text{s}$ in the cavity (having traveled an equivalent of 3 km through the sample), while photons arriving at $100 \mu\text{s}$ have travelled a distance equivalent to 30 km through the sample. The distance travelled in the ring-down time, the characteristic residence time of a photon in the cavity, is conventionally termed the “effective pathlength” and can be calculated from Eq. 2. The second consideration is that the mirror reflectivity changes with wavelength (see Fig. 3, noting that the transmission of the mirrors is proportional to $(1 - R)$). This implies that photons of different wavelengths have different ring-down times, as seen in the non-exponential behaviour of the ring-down curve (Fig. 2), and thus different “effective pathlengths”. A third consideration is that the presence of additional absorbers or extinction processes results in a shorter ring-down time in the system. The measurement of changes in the ring-down time is the basis of the CRDS approach, and a shorter ring-down time implies a shorter (wavelength-dependent) “effective pathlength”.

There is no doubt that the authors appreciate these points, but for the above reasons, we believe the concept of the “pathlength” in the cavity is ill-defined. We think it preferable to characterise a broadband cavity system based on the mirror reflectivity spectrum and the separation of mirrors, which (ideally) do not change during an experiment. Where the term “effective pathlength” has value is as an intuitive figure of merit – for instance, when comparing the sensitivities of this type of spectrometer to other systems, such as a long-path DOAS system. We have recently described (Gherman *et al.*, 2008) how additional extinction processes (scattering and absorption of gases and particles) affect the sensitivity of the technique (or “pathlength”), and discussed the implications for system design, particularly for optimising the cavity length and mirror reflectivity. The effect of additional extinction processes can be adequately described either in terms of the photon lifetime in the cavity or, since the current technique does not use the ring-down principle, in terms of losses per pass in the cavity. In the latter case, we recognise that photons are lost from the cavity both by transmission through

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the mirrors (the $1 - R$ term) and by absorption and scattering in the sample; more rapid losses of photons from the cavity result in fewer contributions from photons that travelled longer distances in the cavity.

Background extinction and concentration retrieval

A central point of the paper by Meinen and co-workers is that Eq. 3, which was derived by Fielder *et al.*, 2003, in the first paper describing the technique, does not properly account for changes in the sensitivity of the technique in the presence of other extinction processes and that a correction is required to account for changes in the effective pathlength. We show below that Eq. 3 is correct when the *absolute absorption*, as opposed to the *differential absorption*, is used to quantify a given gas.

Consider how α changes in Eq. 3 in the general case when we have a total sample extinction coefficient, ε_T , made up of a background extinction coefficient, ε_B , together with the absorption coefficient, α' , of a species whose concentration we wish to quantify:

$$\varepsilon_T = \varepsilon_B + \alpha' = \left(\frac{I_0 - I}{I}\right) \left(\frac{1 - R}{d_0}\right) \quad (\text{C1})$$

These extinction processes can be thought of as contributing separate fractional changes to the intensity: ΔI_ε from the background extinction (which reduces the intensity from I_0 to I_B); and ΔI_A from the molecular absorption (which further reduces the intensity from I_B to I). Solving for α' gives:

$$\alpha' = \left(\frac{\Delta I_A}{I}\right) \left(\frac{1 - R}{d_0}\right) + \left(\frac{\Delta I_A}{I}\right) \left(\frac{\Delta I_\varepsilon}{I_B}\right) \left(\frac{1 - R}{d_0}\right) = \left(\frac{\Delta I_A}{I}\right) \left(\frac{1}{L_{NEW}}\right) \quad (\text{C2})$$

Here L_{NEW} is the new “effective pathlength” when other extinction processes are significant. L_{NEW} can be compared to the “effective pathlength” of Eq. 3 which contains no extinction processes besides the sample absorption:

$$L_{NEW} = \frac{L_{OLD}}{1 + \epsilon_B L_{OLD}} \quad (C3)$$

where we have defined $L_{OLD} = \left(\frac{d_0}{1-R}\right)$. Note that L_{NEW} and L_{OLD} are both functions of reflectivity and hence wavelength. Use of Eq. C1, which is a generalisation of Eq. 3, implicitly results in a shorter “effective pathlength” and no correction factor is necessary.

The discrepancy between the two analytical approaches lies in whether the differential or absolute absorption is considered. In the DOAS procedure, $I_{IN}(\lambda)$ is the intensity *after* removing broad spectral features (*cf.* Eq. 8) and corresponds approximately to I_B above. This value is used in the ratio in Eq. 9; on the other hand, Eq. 3 retains the value of the original I_0 . Since I_B is smaller than I_0 , the fractional absorption, $\frac{\Delta I_A}{I_B}$, is proportionally larger than $\frac{\Delta I_A}{I_0}$. This has implications for spectral analysis based on both the differential (DOAS) absorption and the absolute absorption (Eq. 3). As Meinen *et al.* emphasise, the DOAS procedure requires a correction, as given by Eq. 11, for changes in the “pathlength”. (Eq. 11 can be related to Eq. C3 through $c_{NEW} L_{NEW} = c_{OLD} L_{OLD}$ and a Taylor expansion.) In the non-differential absorption approach, careful control must be exercised to estimate the value I_0 and cavity intensities should be normalised based on changes in the light source intensity – that is, before the light traverses the cavity.

Additional comments

1. Underestimation of target gases using Eq. 3

The authors state (p.10668, from line 20) that using Eq. 3 gives rise to an underestimation of target species and cite the work of Langridge *et al.*, 2006, who compared NO₂ measurements with their broadband cavity spectrometer against a standard chemiluminescence NO_x detector. Langridge and co-workers attribute most (but not all) of the discrepancy to positive interferences arising from or-

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ganic nitrates in the chemiluminescence detector. This explanation fully agrees with more recent studies comparing chemiluminescence NO_x detectors against other techniques, including DOAS and TILDAS (Dunlea *et al.*, 2007), and LOPAP (Villena Tapia *et al.*, 2008), which have demonstrated that chemiluminescent detectors are susceptible to significant positive and negative biases.

2. IBBCEAS, BBCEAS, SC-CEAS, W-ICOS, or CE-DOAS?

The system described by Meinen *et al.* works on exactly the same principle as that described by Fiedler and co-workers, 2003, and other papers from the Cork and Berlin groups, as well as papers from Ball *et al.*, 2004, and the Cambridge group. The proliferation of acronyms for the same technique – “IBBCEAS” (Cork, Berlin and Grenoble groups), “BBCEAS” and “SC-CEAS” (Cambridge group), the similar “W-ICOS” (Thompson and Spangler, 2006), and now “CE-DOAS” (Meinen *et al.*, 2008) – is undesirable as it obscures the fact that the same measurement principle is used. Of relevance to the label “CE-DOAS”, it is worth noting that analyzing the spectra on the basis of the differential absorption is neither (a) novel (Langridge *et al.*, 2006) nor (b) necessary (Venables *et al.*, 2006; Gherman *et al.*, 2008; Triki *et al.*, 2008) with this experimental approach.

3. Calibration of mirror reflectivity using a broadband ring-down transient

Meinen and co-workers describe a new approach to calibrating the mirror reflectivity in the system by recording the ring-down decay of their (broadband) LED in the cavity. This approach is appealing as it would allow *in situ* calibration of the instrument without the practical difficulties associated with calibration gases or the uncertainties involved in other approaches. However, a single exponential does not adequately describe the ring-down transient (Fig. 3) and therefore is not well suited to characterizing the system. The observed multi-exponential behaviour is expected as the transmission curve changes by about 20% to 30% between 650 nm and 670 nm. The analysis is further complicated because even diode

laser ring-downs display a significant variation in decay times depending on the transverse modes being excited, possibly arising from non-uniform losses across the mirror surfaces (Triki *et al.*, 2008). While a multi-exponential function gives a good fit to the measured decay curve, the multiple ring-down times that result cannot be unambiguously assigned to particular wavelengths – that is, it would be impossible to obtain a reflectivity spectrum from the transient without additional assumptions being made. One possible solution to this problem may be to assume that the shape of the reflectivity curve remains more or less constant. If known from the outset, it may be possible to use this shape as a weighing factor in the exponential decay curve to then calculate a modified reflectivity spectrum. In this case, it would be possible to scale and offset the reflectivity spectrum (retaining the same shape) to more fully characterize the mirrors. Whether this suggestion provides a justifiable method of calibrating the system remains to be seen.

The adoption of broadband methods that use the enhancement of the light path in optical cavities shows much promise for monitoring numerous species at small spatial scales and we look forward to seeing more atmospheric groups use this approach.

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