Atmos. Meas. Tech. Discuss., 1, S134–S139, 2009
www.atmos-meas-tech-discuss.net/1/S134/2009/

Atmospheric
Measurement
Techniques
Discussions

Interactive comment on "Broadband Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS) – applicability and corrections" *by* U. Platt et al.

Anonymous Referee #2

Received and published: 2 February 2009

General Comments:

This paper describes the theoretical operating principal behind a new instrument using cavity enhanced absorption spectroscopy. The paper follows on a description of the instrument itself, which appeared in ACPD in 2008 (Meinen et al.). The two papers may be regarded as companions since the first makes reference to this paper for quantitative reduction of data.

The general topic of this paper is of substantial interest, no so much because the technique of cavity enhanced absorption is itself new, but because the paper outlines a method by which a true open path instrument of this type may be operated, i.e., in which the background light intensity at the detector (i.e., the intensity in the absence of absorbing trace gases, or I0) is not known. This is akin to the operating principals of DOAS instruments, in which the variation of the background intensity with wavelength is taken as a slowly varying function of wavelength so that the more rapidly varying trace gas absorptions may be fit without a separate measurement of I0, which is generally not possible in a long path DOAS arrangement.

That said, there are, in my opinion, several difficulties with the mathematical development presented in this paper. Some sections are either incorrect (to my understanding, at least) or else not sufficiently clarified so as to be readily reproduced by the reader. Furthermore, there is insufficient justification for some of the approaches used. For example, the main thrust of the paper is to apply the formalisms conventional to long path DOAS to the mathematical development of a formalism for cavity enhanced absorption spectroscopy (CEAS). Long path DOAS instruments operate with a fixed path length that allows ready separation of background intensity from intensity variation due to trace gas absorption. In cavity enhanced spectroscopy, the light path between two highly reflective mirrors is not a fixed quantity, a fact that forces somewhat different mathematical treatment. This paper defines the path length for CEAS in an averaged sense, and then uses this concept to draw analogous relationships between CEAS and DOAS. The approach appears to obscure, or at least disregard, a simpler mathematical treatment for CEAS already available in the literature, and the reasons for the departure with the accepted CEAS formalism require better justification than is given here.

I would certainly invite a response and further discussion on these points and on the more specific comments below. As stated above, I feel that the general topic addressed here is substantive, and if my criticisms are incorrect or based on a misunderstanding of the mathematics, I would happily see them corrected. In this case, some response to the points below and some clarifications on certain other points would make the manuscript acceptable for publication.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Specific comments:

Page 484, minor comment on equations 1-5: The quantities given in these equations are all wavelength dependent (i.e., R, rho, etc.) and it would be helpful if that were explicitly noted at the outset, i.e., that the development given here and in the following equations is for a single wavelength point in a spectrum, and the spectral dependence is considered at a later point in the paper. It is also worth pointing out here that the "average" path is identical to the 1/e path length for an exponential decrease in light intensity with path. The latter is the more conventional terminology, though the two are equivalent.

Page 485, equation 6: The equation includes only a loss term and no source for light entering the cavity from an external source, which seems to be the case that describes the broadband spectroscopy apparatus. As written, the equation would more appropriate for describing a ring-down apparatus than a spectrometer with a continuous (rather than pulsed or modulated) light source.

Page 486, equation 13: This is the same as equation (5) on page 484, which was given by inspection. Some condensation of the development would seem appropriate here to reduce the number of equations.

Page 487, equations 14-15. These are confusing, as are the curves drawn in Figure 2. For example, the quantity Iin0(n) is not given in Figure 2, though there is a quantity Iin(n0) in the figure. Are these the same? It is also not clear what the distinction between n0 and n is in the figure caption. Is n0 intended to mean zero passes, or simply an arbitrary number of passes after the light intensity has begun to decay from the cavity? In either case, there appears to be some duplication or lack of clarity over the "0" subscripts on either the intensities or the pass numbers that make the figure and the equations difficult to understand. It would be helpful if the authors could clarify these points.

Also, what does the "+" sign mean in equation (15) ?

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Page 488, equations 17-18: The quantity DCE is not well defined. Presumably, this is the observable quantity, and is intended to mean the logarithm of observed ratio of background intensity (no absorber) to signal intensity (absorber present) outside of the optical cavity. This is not explicitly stated. It is given either after n traverses or as the integral of an intensity decay. The latter would seem to be correct (equation 18), though not equivalent to the intensity ratio at a given point on a decay (equation 17). The two definitions for DCE seem to be inconsistent, so that the definition of which DCE is actually used later in the paper should be clarified. In either case, the intensity is taken as one that only decays from the cavity, rather than as one that has both a source term and a decay term, as in a real CEAS experiment (see comment above). It appears that equation 18 is actually what is used beyond this point, which I have taken to mean the logarithm of the observed intensity ratio without and with the absorber.

In this case, equation 18 is given as an equality between two logarithms, i.e.,

ln(I_0/I) = ln[(rho_0+tau_0)/rho_0)]

There should be an explanation at this point as to why the logarithms are needed. The equality between the arguments of these logarithms is identical to the treatment of cavity enhanced spectroscopy already in the literature (see for example, Fiedler references cited herein). One could arrive at equation 18 simply by taking the logarithm of both sides of equations already derived in the literature, assuming that my interpretation of the meaning of the integrals given in equation 18 is correct.

Page 488-489, limits of DCE. I was not able to reproduce the first limit given here. A plot of DCE against tau for realistic values of rho_0 and tau would perhaps be useful to demonstrate where this limit is actually achieved. Using, for example, rho_0 = 10-6 and tau = 10-4 for case 1, DCE = 4.62, not close to the limiting value of 2 given here. Increasing tau does not bring the limit any closer to 2 and does not result in a constant value. If indeed this limit is not correct, the statement on page 489 (and later) that high mirror reflectivity is problematic is not well justified.

Page 489, equation 21: This is a different expression for DCE that does not seem to be justified by the equations leading to this point. It states that the logarithm of the intensity ratio (i.e., DCE) is directly proportional to the product of the average path length and the optical extinction coefficient, i.e.

DCE = ln(I_0/I) = L c sigma = L epsilon

Where here L is the average path length defined in the paper (L bar) and c the average concentration (c bar). Using the previously given expressions for average path length (i.e., equation 13), and the previous definition for DCE (equation 18), I am not able to reproduce the expression in 21 (also used again, for example, in 23). If the equation is correct, its meaning needs to be clarified. Perhaps, for example, this equation is not intended to relate the average path length in (13) to the definition of DCE in (18), or perhaps this DCE is different than that given in (18). Either way, this equation needs clarification.

Page 491, equation 26: This equation is based on the above relationship, and follows directly if equation 21 and 23 are indeed correct. If so, this would seem to be the end point of this paper, since it gives an analytical expression for the desired quantity, the trace gas concentration. Identical expression using the ratio of DCE/(1-DCE) are then given by other methods in the following pages, which seems redundant. Some condensation of this material seems possible?

Pages 495- 497, section 5: The direct comparison of CEAS to DOAS here is useful in the sense that background intensity, I0, is not necessarily easily determined in an open path CEAS configuration, just as it is not determined in DOAS, but rather fit as a slowly varying component with wavelength. Solutions 1 and 5 addresses this issue, whereas solutions 2-4 address the important, but separate issue of determining total cavity loss. These discussions should be distinguished.

Summary:

The paper suggests the substitution of the linear relationship commonly used in CEAS to derive trace gas concentrations from measured changes in intensity outside of an optical cavity with a logarithmic relationship that more closely resembles Beer's law. Though the substitution would be useful if it would allow applications of DOAS conventions to CEAS, the development is difficult to follow and requires either clarification or revision. The literature expression for the intensity change given in various references (e.g., Fiedler and coworkers) is, using the notation of this paper:

(I_0-I)/I = [(1-rho)/d_0] c sigma

It is true that replacement of this relationship with a logarithmic one results in a non-linear relationship between the "optical density", ln(Io/I), and the trace gas concentration, c. The advantage in surrendering the linear relationship is not clear from this paper but could perhaps be made clearer from a more explicit comparison to the above equation. Lastly, it is noteworthy that nowhere in the above equation is there an explicit need for a path length. Only the cavity loss due to mirror loss, Rayleigh scattering (and Mie scattering, if particles are present) needs to be known. While there is no question that the effective path length associated with these cavity losses is variable and would change as the absorber concentration changes, it is not necessary to know, or to correct for, this variation to derive a concentration. Again, it would seem some further justification on the explicit use of path length to derive concentration where is it not otherwise required should be given.

Interactive comment on Atmos. Meas. Tech. Discuss., 1, 481, 2008.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper