Atmos. Meas. Tech. Discuss., 4, C202–C206, 2011
www.atmos-meas-tech-discuss.net/4/C202/2011/

Atmospheric Measurement Techniques Discussions

Interactive comment on "Diode laser-based cavity ring-down instrument for NO_3, N_2O_5, NO, NO_2 and O_3 from aircraft" *by* N. L. Wagner et al.

Anonymous Referee #1

Received and published: 27 March 2011

General Comments: The article "Diode laser-based cavity ring-down instrument for NO3, N2O5, NO, NO2 and O3 from aircraft" by Wagner, et al. describes an impressive new tandem instrument that combines several types of chemical and thermal modulation with two robust optical measurements (of nitrate radical and nitrogen dioxide) to produce determinations of five key atmospheric species suitable for airborne sampling. This impressive achievement is described reasonably well (except for a few problem sections that I identify below) with a careful description of most of the conceivable problems and limitations. What is missing is an overall assessment of the measurement capabilities (limit of detection, measurement precision and accuracy) of the instrument as deployed in the CalNex field measurements. I understand that capabilities have a tendency to improve with time, but there appears to be enough data from the flights and preflight experiments to provide a detailed characterization of the instru-

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

ment as it was in June 2010. Specifically, I'll highlight the statement in the Abstract "The measurement precision for both NO3 and N2O5 is below 1 pptv (2σ, 1s) and for NO, NO2 and O3 is 170, 46, and 56 pptv (2σ, 1s) respectively." since these specifications are (or seem to be in the case of the latter three measurements) detection limits based on optical-only deviations in the zero baseline, which is only minimally related to the overall uncertainty of the instrument (at least for NO3 and N2O5). My comment is based on an assertion (using quoted effects within the paper) that the uncertainty associated with the actual measurement of optical loss within any of the measurement cells is one of the smallest contributors to the overall uncertainty of the measurement. I'll note some specific areas of concern in the next section, but I wish to close with the statement that this is a good paper and that the uncertainty issue can easily be addressed in an edit and that I recognize that the reported instrument appears to be working quite well in the challenging airborne measurement situation.

Specific Comments: An interesting question (in my opinion) is whether the incorporation of the relatively broad-band diode laser sources into the CRD measurement really resulted in an improvement of the instrument. Note that this issue can be considered in isolation from the other revisions to the instrument that allowed for the three NO2-related determinations.

Clearly, in the case of the shift from 532 nm to 405 nm, a significant improvement in the nitrogen dioxide measurement was realized based on the increase in the effective absorption cross section and avoidance of ozone interference (and probably the breadth of the spectral features/spectral filling under the diode laser bandwidth). It is interesting that there is an unexpectedly (?) strong dependence on pressure observed in the NO2 channels and some suggestion of the origin of this effect would be useful. With the proviso that the pressure dependence is properly represented and is relatively constant, the move to a diode laser appears to have improved these measurements.

On the other hand, the move from a narrow-band dye laser source to the diode laser appears to have significantly degraded the NO3 measurements. One aspect is that the

AMTD

4, C202–C206, 2011

effective absorption cross section is smaller, due to the incorporation of less strongly absorbed wavelengths into the ring-down signal. More problematic (in principle) is the suggestion that non-exponential ring-down decays are observed. This is attributed to the presence of underlying water absorptions, but in fact, the variation of absorption cross section within the bandwidth of the diode laser can result in multi-exponential decay signatures (the decay rate of some photons is larger than others). This could also be a problem in the NO2 measurements, but is apparently not observed? Even more problematic is that possibility that the active mode structure produced by the diode lasers might change with time. Note that these effects would probably not be observed in an empty cavity unless there were large enough differences in the losses of the different cavity modes excited, so the Allan analysis might not have been useful in characterizing the problem.

I'm not sure how important the discussion in the second paragraph (line 4) on page 1568 is, since the reactions that drive NO and ozone into NO2 are probably quantitative, but that paragraph is very difficult to understand. I read it carefully several times and I still am not sure that I understand the argument. Please rewrite this to make it clearer.

The discussion that spans pages 1575 and 1576 appears contradictory, hearkening back to the comment above about global uncertainty. The pptv levels quoted in the Abstract for NO, NO2 and O3 are cited as detection limits but then 100 to 300 pptv drifts are cited as a problem. If the drift has been characterized and is linear (or at least deterministic) I could see how it could be included in the background subtraction procedure and would thus be a minor contributor to the uncertainty. Is this the case?

There are number of contributions to the uncertainty of each of the measurements that should be considered in quoting the accuracy and precision of the instrument: for example, the conversion of N2O5 to NO3, the transmission (and the variation of the transmission during use on short and longer time-scales) of NO3 to and through the measurement cell, and the uncertainty of the absorption cross section at elevated

AMTD

4, C202–C206, 2011

temperature all contribute to possible inaccuracy (and in some cases imprecision) of the dinitrogen pentoxide concentrations determined. A similar analysis should be conducted for each of the analytes. I believe that Dube and Brown have worked through these analyses to produce valid figures of merit for the older instrument, so it should be possible to follow their template. Since the Abstract represents a synthesis of the results of the paper, it would be more appropriate to quote the better, more global characteristics there.

Technical Corrections: In both of the corrections (for water and pressure) second order polynomials are used, not third, as is stated in the text and figure captions.

An inset to Fig.1 showing the zero air / inlet combination would be helpful in visualizing it.

Likewise, the discussion on line 12, page 1573 would be clearer if Fig. 1 showed the heater and NO inlet and the text said that the heater was followed by the NO addition (before the nylon NO3 scrubbing). I assume that is what is going on: 1) add NO to turn ambient NO3 into NO2 or 2) heat and then add NO to turn NO3 from ambient+N2O5 into NO2. If the conversion of NO3 by NO is quantitative, why is the scrubber even needed? (If it isn't quantitative, isn't there a larger problem?)

I assume that all tubing in the system is Teflon? It would be prudent to say this from the outset, since materials (and the word tubing) are otherwise omitted in many places.

Line 5 on page 1571 isn't very clear. There are stated uncertainties of 1.5, 4, and 6% for what appears to be the same thing. Also, when heated, the absorption cross section for NO3 changes – presumably the uncertainty also increases?

The caption for Fig. 8 is wrong as regards the colors.

The suggestion that elimination of methanol-based dye solutions was a major increase in safety for an instrument that generates ozone and carries high pressure zero air and NO (and solid N2O5?) is a bit dubious.

AMTD
4, C202–C206, 2011

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 1555, 2011.

AMTD

4, C202–C206, 2011