

Interactive comment on “A broadband cavity ringdown spectrometer for in-situ measurements of atmospheric trace gases” by M. Bitter et al.

Anonymous Referee #2

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General comments:

This is a clearly written paper describing an important new measurement capability for NO₃, N₂O₅, I₂ and OIO. The broadband CRDS method is an interesting and novel approach to trace gas measurement that may offer some advantages over more conventional CRDS methods. It has been described previously, but I believe this is the first demonstration of the technique as part of a field campaign. This manuscript mainly describes the operation of the instrument itself and the retrieval of mixing ratios of the different compound. The forthcoming paper (Bitter et al, in preparation) on the field measurements themselves should also be very interesting.

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The major advantages to the broadband CRDS technique include its versatility, which comes from the ability to combine DOAS techniques with CRDS and to shift between different spectral regions. This is illustrated by the detection of OIO and I2, not previously measured by CRDS in the atmosphere, within the same data set as detection of NO3 and N2O5. Also, the measurement in an open air cavity is clear advantage over some previous examples of CRDS (e.g., Brown et al), which require filtering the air sample to suppress noise due to aerosol scattering. The disadvantages to the broadband method arise mainly from the deconvolution of interference from water vapor. The resolving power of the grating spectrometers used to disperse the output of the ring down cavity is insufficient to suppress bandwidth effects that complicate the interpretation of ring-down signals for narrow band absorbers such as water vapor. The manuscript goes into some detail on this point, and it appears that the authors have treated this problem rather thoroughly and are able to accurately deconvolute the spectra. Nevertheless, this seems to remain the most important issue with the measurements.

Specific comments:

The first reviewer made several very good comments, and I would agree with much of that review. I won't repeat any similar comments here but will add a few additional ones.

1. Page 3498: Acquisition of a zero for NO3, OIO or I2. This is accomplished by insertion of a glass tube in the open path of the cavity and then flushing the cavity with dry nitrogen. This procedure seems somewhat cumbersome and potentially problematic. First, nitrogen and air have different Rayleigh scattering cross sections. The cavity ring down instrument should be sensitive enough to detect this difference in an atmosphere of either gas. Does the difference matter to this measurement? Why not simply use zero air rather than nitrogen? Second, does insertion and removal of the tube affect the alignment of the cavity and therefore the ring down time constants? Third, how frequently does this zero need to be taken in order to stay ahead of any drifts in the zero

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due to, for example, thermal drifts in the mirror mounts that may affect the alignment (particularly for an open air cavity subject to daily ambient temperature fluctuations.) Is it the case that the combination of DOAS with cavity ring-down reduces the need for frequent zeros? If so, the point is not made clearly (at least to my reading) in the manuscript. Some further comment on all of these points would be helpful.

2. Page 3499: Measurement of the sum of $\text{NO}_3 + \text{N}_2\text{O}_5$. There are three factors that the authors consider to derive this concentration in the closed cell arrangement: dilution by the purge flow (1.36), incomplete conversion of N_2O_5 (1.05) and wall loss (1.38). Does this mean that the total signal must be multiplied by a factor of $1.36 \times 1.05 \times 1.38 = 1.97$? This number and its uncertainty should be given in the manuscript. Also, there should be some comment on the choice of 60°C for N_2O_5 conversion rather than a higher temperature where this reaction would go to completion. Also, some comment on the choice of a flow rate of 1900 SCCM, where both dilution and wall loss are rather significant. Why not a larger flow rate?

3. Page 3512-3513: Time resolution. The chosen time resolution of 100 s, while clearly an improvement over the data presented at 42 min, is still not really fast enough to capture "rapid" variability in a compound such as NO_3 . Some further comment on the goal of the measurement might clarify this point. For example, 100 s is likely sufficient to capture large scale changes due to shifts in air masses at the measurement site, but not likely enough to capture variability arising from smaller scale changes such as, for example, deposition or highly localized emissions of sink compounds.

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