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Atmospheric Measurement Techniques
Discussions

Interactive comment on “Thermal dissociation cavity ring-down spectrometer (TD-CRDS) for detection of organic nitrates in gas and particle phase” *by* Natalie I. Keehan et al.

Anonymous Referee #2

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Keehan et al. describe the adaptation of a commercial CRDS NO2 instrument for measuring classes of thermally labile nitrates in both the gas and particulate phases. The thermal-decomposition technique for measuring classes of nitrate compounds has been an important tool for constraining concentrations of unknown nitrate species and e.g. NOx / NOy budget closure studies. Typically, these types of measurements have been demonstrated using custom-built NO2 sensors, and it is therefore quite useful to show that a commercial NO2 sensor can also be used to produce sufficient data quality for e.g. laboratory and urban studies.

The paper is well written and thorough and I think deserves publication in AMT after addressing some suggestions and questions that I outline below. I do think there are some important issues that the authors should address in the revision. These are listed in the specific comments below but I will reiterate them here:

1) Why is the inlet transmission of N2O5 believed to be so low and how do we know that the inlet transmission for other species, e.g. HNO3 or AN, is not also low? NO2 and particulate RONO2 are somewhat validated by comparison to other instruments, but I do not believe that absolute standards of other species are presented. 2) Please carefully check figure 5 and the discussion surrounding the thermal decomposition of N2O5 and NO3, as discussed below. 3) How could a pressure reduction upstream of the heaters change the recombination of thermally decomposed species?

Line 23: I’m not sure why the word “oxidized” is here.

Line 65-67: Molybdenum catalysts are also widely recognized to convert some other NOy species, not just NO2, into NO, which would cause a significant problem for this work.

Line 67-68: I would say for LIF the limit is laser power not cavity length. A Multipass cell essentially increases laser power in the middle of the cell.

Line 78: remove first word

102-104: I was confused by mentioning LGR CRDS with two flow rates. Recommend clarifying that the two are different instruments and that the second one is for the present work.

106: Metric units please

135: It seems likely the settling time might be significantly reduced by maintaining flow through all channels at all times. Recommend the authors consider this for future deployments, or comment in the manuscript of they know that this would not help.

145: Is there ever any aerosol NO_2 detected or could this sampling mode be eliminated?

Section 3.1: Can you say a bit more about how the comparison with the commercial NO_x sensor was performed? Was this performed over a short time period by dynamically diluting air from the lab which is expected to be a relatively constant mixture during the experiment? If so, any interference would not be a constant offset but would scale with the dilution. I am actually surprised that the slope is so close to 1, as I expected that the molybdenum converter converted many NO_y species. Conversion of Nitric acid seems like another likely positive interference with the CL instrument. It may be that that sensor reports 0.64 ppb even when sampling clean zero air due to a background from the converter. How is the zero for the CRDS determined? Is the laser tuned off of an NO_2 resonance or is a periodic zero air sampling period required?

174: In my experience, the certification on those cylinders is not good for more than 1 year and significant loss of NO_2 in the cylinders is sometimes observed over longer periods. Perhaps this one is different.

Line 188: "delta-3-carene"

Section 3.3 / Figure 4: How is it known that the observed thermogram from $\sim$50 – 100C (PNs) is from peroxy nitrates and not from N_2O_5? Can the authors cite a paper showing that the formation of peroxy nitrates are expected from the reaction of D-3-carene + NO_3?

Section 3.4 / Figure 5: I am confused by this figure. The gray line shows much more noise than the black, and when I first looked at it assumed the gray line was for the low oxidant experiment although now see that the caption suggests otherwise. The precision shown on the black line against the left axis seems better than is expected for the stated detection limit of the CRDS instrument. So – can the authors please check that the legend and axes are labeled properly? If they are reversed this would change some of the discussion. Also, for the low oxidant experiment, as shown on the

left axis, the thermogram shows a > 5 ppb range of NO_2, while the caption says that 3.2 ppb was used. Could the authors provide a bit of discussion here surrounding what is expected from the experiment, e.g. is it expected that in the low oxidant experiment all of the NO_2 would be lost to the NO_3 + alkene reaction by the time the air is sampled by the instrument, and so we should expect to see about as much $RONO_2$ as there was initially NO_2?

I was somewhat confused by the discussion surrounding the appearance of N_2O_5 in the thermograms. Initially I thought that the authors were suggesting that $N_2O_5 \rightarrow NO_3 + NO_2$ was resulting in the increase in signal > 200C, but later realized they were talking about $NO_3 \rightarrow NO_2 + O$. I suggest this section starts with a brief discussion of the two-step thermal decomposition of N_2O_5, and I would not refer to $NO_3 \rightarrow NO_2 + O$ as thermal dissociation of N_2O_5. Could the authors indicate where $N_2O_5 \rightarrow NO_3 + NO_2$ is visible in the thermogram? Also, what effect is there from thermal decomposition of O_3 followed by $NO_3 + O \rightarrow NO_2 + O_2$?

I am quite surprised by the very low transmission / detection of N_2O_5 in the system, as I would not have thought based on the previous similar studies that N_2O_5 was much more difficult to sample than the other classes of nitrates. The stated detections in the PN and AN channels (7% and 28%) are difficult to reconcile. If N_2O_5 is completely dissociated in the PN channel, and the conclusion is that only 7% of N_2O_5 must be transmitted through the inlet, than I would expect at most another 7% of signal from the NO_3 decomposition (total of 14% instead of 28%). But still, in the AN channel only a fraction of NO_3 is dissociated. Did I miss something here? Is there another study that could be cited that reports low transmission of N_2O_5 through Teflon tubing?

Section 3.7 / 3.8: The dependence of the inlet heater conversion efficiency and chemistry on the pressure within the heater is not discussed, but may be worth consideration for the authors in the future. My expectation is that if a lower pressure is used within the heater, this would greatly reduce the recombination. Perhaps it is not used that way here because this would require lower pressure within the CRDS and possibly lower precision. If so, it is a worthwhile point of discussion when considering differences between CRDS and LIF detection of NO2.

Line 284: please include the Knopf et al citation in the Reference list. Also, I presume that the OH loss rate was calculated based on the uptake coefficient stated in that paper using the conditions for this experiment. If so, I suggest the authors state that here because as it is it sounds like the 46 / s number came directly from that paper.

Section 4.1: Were any particulate peroxy nitrates detected using the TD-CRDS instrument? Is it known how those would be classified by AMS?

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