

Interactive comment on “Evaluation of the accuracy of thermal dissociation CRDS and LIF techniques for atmospheric measurement of reactive nitrogen species” by Caroline C. Womack et al.

Anonymous Referee #2

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This manuscript presents a set of experimental data investigating the thermal dissociation of NO_y species into NO₂ (e.g. HNO₃), with subsequent detection by CRDS and LIF. They report detailed experiments (at different temperatures) on the dissociation of HNO₃, NH₃, N₂O₅ and ammonium nitrate, all of which are either NO_y species of atmospheric relevance (in the case of HNO₃), or potential interferences in a total NO_y instrument (in the case of NH₃). The experimental work is backed up by a chemical model which does a good job at reproducing the observed thermal decomposition. The work is well presented, reasonably thorough and will of no doubt be of great interest to anyone wishing to make a total NO_y measurement using the thermal decomposition

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method. I would recommend publication in AMT subject to the authors answering the following comments and questions.

Could the authors explain why they did not carry out experiments using common atmospheric NO_y constituents such as peroxy and alkyl nitrates? Clearly these are likely to fully dissociate at the highest temperatures and this has been shown in previous work on the TD-LIF instrument, however it would have been good to actually see this shown experimentally. A thermogram of n-propyl nitrate from the UC Berkeley TD-LIF instrument is shown but it would have been nice to have seen this for the TD-CRDS system as well (especially considering one of the conclusions from the work is that all ovens behave differently). I do not know if the authors intend to use their system to provide NO_y class speciation in their atmospheric measurements (and hence need to know the thermograms for PNs and ANs), however others may wish to and would therefore be interested to see this.

It would also have been good to have seen the conversion at different levels of NO and NO₂ in the initial sample, corresponding to what would be the case in ambient measurements. Would the authors expect any difference in behaviour of the inlet with different NO_x levels (e.g. any NO to NO₂ conversion)?

Having read the title of the manuscript, I did find myself disappointed at the lack of results shown from the TD-LIF instrument. In reality this seems to be a paper that describes work done on the TD-CRDS system with a single set of results of HNO₃ dissociation from the TD-LIF shown as an example of how two apparently similar systems can behave differently. This is fine and doesn't particularly detract from the results, however maybe the paper title is a bit misleading?

I found the section on ammonium nitrate conversion very interesting. It has often been a question when looking at total NO_y measurements by some form of conversion to NO or NO₂ as to how much nitrate aerosol is converted and this work goes some way to answer this. I wonder if a recommendation from the work could be that steps should be

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taken to remove aerosols from the system (e.g. using a cyclone or something similar) if purely gas phase NO_y is of interest? Maybe this could also be run sequentially to give an actual measurement of particulate nitrate? Could the authors make any comment on how other particulate nitrate (e.g. organic nitrate) would behave in the system? I would imagine there are situations when organic nitrates could make up a large proportion of the total particulate nitrate and so how these are converted would be of great interest.

Could the authors include a summary plot showing the thermograms of all the different species? Maybe this would look too busy but it would help the reader to understand the temperature that different conversions and interferences occur.

Minor corrections:

P2 L20: the authors could also include mention of GC-MS to measure organic nitrates (e.g. Worton et al., Atmos. Env. 2010) in their list of NO_y techniques.

P4 L19: Are there any examples of using TD followed by photolytic conversion / chemiluminescence to detect the NO₂?

P5 L28: How are the known concentrations of NO₂ produced (e.g. GPT, standard bottle with dilution)??

Figure 4: It would be better if these were plotted as a % conversion to NO₂ as is done for all the other figures.

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