

The authors would like to thank the reviewers of the manuscript entitled “Evaluation of the accuracy of thermal dissociation CRDS and LIF techniques for atmospheric measurement of reactive nitrogen species” for their helpful comments and suggestions. Our responses are as follows. The reviewer comments are in italics, our responses are in regular font, and changes to the manuscript are in blue.

Reviewer #2

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.

The reviewer is correct that it is well worth looking at the conversion efficiency of peroxy and alkyl nitrates in a TD-CRDS instrument. Although we do not plan to use the TD inlet at intermediate temperatures for NO_y speciation, others may, and we direct interested readers to the excellent paper by Thieser et al. (2016), which covered this topic nicely. We restricted our attention to quantification of the unintended thermal dissociation of HNO₃ at temperatures commonly used to measure ANs, and thus did not attempt to re-measure the conversion efficiency of PNs and ANs.

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 behavior of the inlet with different NO_x levels (e.g. any NO to NO₂ conversion)?

We appreciate and share the reviewer’s concern. Please see our response to Reviewer #1’s comment on P11L9

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?

We understand the reviewer’s concern, and it is true that this manuscript largely focuses on CRDS, but we would still prefer to retain LIF in the title, as it encompasses the results obtained by two of the paper’s coauthors.

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 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.

Thanks to the reviewer for this suggestion. An impactor or cyclone could be used to eliminate particulate ammonium nitrate, whereas a heated aerosol sampler could potentially be used to sample 100% of the particulate matter in aircraft studies. As for other particulate nitrates, it seems likely that organic nitrates would be driven into the gas-phase with the same efficiency in our oven, given the results of Rollins et al

(2010), and therefore would undergo complete conversion, but further tests would be required to test this. We have included lines in the discussion section which address these two issues. P19L24 now reads: “Their results indicate it is likely that particulate organic nitrates would be converted to NO₂ with 100% efficiency in the NOAA TD-CRDS, but this result has not been explicitly tested here.” Additionally, P20L1 now reads: “In future studies, a TD inlet that either effectively samples aerosol, or effectively excludes aerosol (such as a cyclone), or a combination of the two could be used to specifically measure aerosol nitrates, which may make up a substantial fraction of NO_y, particularly in polluted wintertime urban atmospheres.”

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.

Yes, we can do this. We have put it in the supporting documents as Figure S8.

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.

Thank you for this suggestion. We have included the Worton paper from 2008 which introduced this technique in the introduction. (P2L33)

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

As far as we know, the only example of TD-chemiluminescence is Perez et al (2007), which dissociated HONO to make NO. We are not aware of any groups using TD-chemiluminescence to detect NO₂ directly. Because the line referenced here was only discussing techniques which generate NO₂, we didn't include that reference here, but did include it later in that section.

P5 L28: How are the know concentrations of NO₂ produced (e.g. GPT, standard bottle with dilution)??
Please see our response to Reviewer #1's comment on P5L23

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

We have changed figure 4 accordingly.