

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 #3

Main comments and questions:

Page 11, lines 4-13: Placing a stainless steel valve in front of the oven is something that I would avoid working with HNO_3 that may be efficiently loss, even if the authors mention a test with the valve fully opened to check if the conversion of HNO_3 changes when it is removed.

It is true that stainless steel should normally be avoided, but Teflon valves did not provide a stable enough pressure to allow us to use them. Therefore, we used a heated stainless steel valve with the minimum amount of surface area possible to avoid any losses. The thermograms were also run over the course of hours to days, so the HNO_3 should have had enough time to come to an equilibrium with the surface.

Page 12, line 3: Authors tested the effect of RH on the thermograph shape of the HNO_3 with a test at 0% and another at 66%. Since in several sites the RH goes up to 90%, it would be worth to have one more point at high RH.

Unfortunately, this would have proved to be technically difficult to achieve, so based on the lack of a difference at 66% RH, we decided not to pursue higher RHs. However, the reviewer is correct that there could possibly be a non-linear water effect that is only evident at very high RHs, so we have included a line which describes this caveat. P12L22 now reads: “Additionally, we did not test the conversion efficiency at very high RH levels, and it’s possible there could be a non-linear effect of water.”

Page 15, lines 7-19: In this paragraph even if not clearly reported, it is implied that the thermal conversion of NH_4NO_3 , reported also in figure 7, is a two step conversion: first from NH_4NO_3 to HNO_3 and then from HNO_3 to NO_2 , since the CRDS measures NO_2 . In this case it would be important the residence time to allow the double thermal dissociation in the heated tube, but this is not mentioned nor explored.

We anticipate that the thermal dissociation of NH_4NO_3 , which takes place at much lower temperature, is rapid. Indeed, our model suggests that the thermal dissociation rate of HNO_3 is also quite rapid, and that the residence time in the heater is required largely to effect the temperature rise in the gas sample and not to allow time for the decomposition reactions. Furthermore, the shape of the thermogram, with a plateau at high temperature matching that of HNO_3 , together with the calibration against an NH_4NO_3 source, indicates complete conversion. We added a line indicating this. P16L3 now reads: “The close agreement between the two thermograms demonstrates that the dissociation pathway is $\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3$, and that this reaction is rapid at the temperatures reached in the TD inlet.”

Page 15, lines 17-19 and figure 7: Here it is reported that the thermograph of NH_4NO_3 agrees with that of HNO_3 reported in fig. 2. In fig. 2 are showed 4 thermographs of HNO_3 , but, to me, none of them are the same reported in figure 7.

The black trace in figure 7 is the same the one shown in gold squares in figure 4. Thank you for pointing out that this was not clear. The figure caption has been updated as “The black solid line indicates the measured thermogram of gas-phase HNO_3 at a 1.9 slpm flow rate (from the gold squares trace in Fig. 2).”

Page 16, line 18: The NH_3 conversion is unimportant for all the TD-LIFs, since all of them measure directly NO_2 : so I would generalize this conclusion to all the TD-LIFs and not only to the Berkeley TD-LIF.

We have made this change. P16L32 now reads: “The interference is only present when O_3 is added to the mixing volume, indicating that the conversion of NH_3 must be producing NO , rather than NO_2 , and is subsequently unimportant to instruments that measure NO_2 only, such as TD-LIF instruments.”

Page 18, lines 22-23: This statement is not correct: 1) there are several campaigns where TD- NO_2 were used during nighttime (i.e. BEACHON-RoMBAS, see Fry et al, 2013; RONOCO, see Di Carlo et al., 2013). 2) There is at least one paper where is described that during nighttime the channel of the TD-LIF instrument that converts total peroxy nitrate into NO_2 , converts also N_2O_5 (Di Carlo et al., 2013). In that paper is reported also the comparison of nighttime measured peroxy nitrate by TD-LIF with the N_2O_5 measured by CRDS, taking the advantage of a TD-LIF and a CRDS installed on the same aircraft. In that work it is also showed that the TD-LIF measurements of peroxy nitrated, during nighttime and at least in the RONOCO campaign, are dominated by N_2O_5 .

Although the design of TD-LIF instruments has traditionally been oriented toward understanding photochemical reaction products of reactive nitrogen, we agree that the original statement was too general. We have rewritten that paragraph to account for studies that did use TD inlets at night. P19L5 now reads: “TD- NO_y instruments often operate in the daytime when N_2O_5 is not a significant fraction of NO_y , though some groups have operated at night and have typically assumed complete conversion to $NO_2 + NO_3$ at the TD inlet setpoint for PNs (Di Carlo et al., 2013), and complete conversion to $2NO_2 + O$ at the setpoint for HNO_3 (Wild et al., 2014). These results confirm that there is approximately quantitative conversion at these setpoints, though there are slight deviations from 100% conversion near the PN setpoint. Therefore, care must be taken to select a setpoint carefully and ensure complete conversion at that temperature. However, this interference would only be significant during nighttime or during very cold weather sampling.”

Minor comments and questions:

Page 6, line 1: the inlet tube 0.39 cm ID. Seems too small, is it a typo or a conversion error from inch to cm?

We used 1/4” tubing, which has an inner diameter of $5/32'' = .39$ cm

Page 15, line 5: Cohen, 2016 is cited as reference here, but it is not reported in the reference list.

Thank you for noticing this. Cohen 2016 was indeed missing. [This has been fixed.](#)