Interactive comment on "Measurement of NO$_x$ and NO$_y$ with a thermal dissociation cavity ring-down spectrometer (TD-CRDS): Instrument characterisation and first deployment" *by* Nils Friedrich et al.

Anonymous Referee #2

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Friedrich et al. describe a 2-channel thermal dissociation cavity ring-down spectrometer (TD-CRDS) for quantification of NOx, NOy, and particulate nitrate (pNit). Thermograms of peroxyacyl nitrate (PAN), isopropyl nitrate and nitric acid are presented. The potential interference from NH3 and secondary radical chemistry is evaluated. The use of an activated carbon denuder to suppress gas-phase components of NOy and transmit pNit is described. Several experiments are presented to characterize the performance of this denuder: the transmission of ammonium nitrate particles in the 10 nm - 414 nm size range and the partial removal of several trace gases (NO, NO2, PAN, iPN,

and HNO3) as a function of relative humidity (RH) which revealed inlet memory effects. Sample ambient air measurements from the 2017 AQABA campaign and ambient air measurements in Mainz, Germany are presented.

This research group has described similar instruments previously (Sobanski et al., 2016; Thieser et al., 2016) and in this paper extends the earlier measurement capabilities to now quantify NOx, NOy, and aerosol nitrate. The measurement of NOx and NOy (including NH4NO3) has previously been demonstrated by Fuchs et al. (2009) and Wild et al. (2014), so that the main novelty of this work is the use of the denuder to selectively quantify ammonium nitrate. A denuder was previously used by the Cohen group (Rollins et al., 2010) to quantify organic nitrates which dissociate at a lower inlet temperature than NH4NO3.

The measurement of NOx by CRDS through the addition of O3 is convincing. However, the paper will require considerable revision before it can be considered for acceptance. I have summarized my major concerns below. Most importantly, I am not convinced that the instrument presented here yields accurate NOy and particulate nitrate data.

Major comments

(1) Thermograms and temperature dependence of thermal dissociation:

(a) The thermograms presented in this paper are inconsistent with literature, but no convincing rationale is provided as to why that would be. (Day et al., 2002; Wild et al., 2014) have shown that thermograms of iPN and HNO3 are considerably offset from each other, which is what one would expect from their Arrhenius parameters (and is shown in the SI of this paper as Figure S2D). The "rather short" heated section of the inlet likely broadens the thermograms which is undesirable but should not have resulted in their complete overlap.

(b) The thermogram for PAN is inconsistent with a large body of literature including work by the Mainz group (Phillips et al., 2013) which showed full dissociation of PAN at an

inlet temperature of ~150 °C (not at ~400 °C). If the higher dissociation temperatures are a consequence of the short heater residence time, then this would be design flaw as the higher temperatures enable unwanted side reactions, increase thermal gradients, and reduce selectivity.

(c) Have the authors independently confirmed the identity, purity and concentrations of the gases they sampled by CIMS (PAN, HNO3) or GC (iPN)? For PAN, Figure S2a shows a step after ~300 °C which may be due to the presence of an alkyl nitrate. For iPN and HNO3 Figure S2 shows "expected values" based on permeation and dilution flows, though I consider these methods reliable standards.

(d) The thermogram of NH4NO3 should be shown.

(e) N2O5, ClNO2, and HONO are important NOy components; their thermal dissociation should have been evaluated since the claim is made that the inlet's behaviour is different from that of Wild et al. (2014).

(2) Denuder performance:

(a) The denuder partially transmits gases but at a rate that appears to be dependent on environmental factors such as RH (Figure 6) and possible also ambient air temperature (not examined). The transmission of many potentially important components of NOz (e.g., N2O5, ClNO2, HONO) was not evaluated but should have been.

(b) Memory effects. The high-concentration experiments described on pg 13 are a poor way of assessing memory effects because there could be a limited number of surface sites that are overloaded when sampling a high concentration. A more realistic experiment would be to sample a low concentration of NOx for a longer time period, and then examine what comes off the denuder while sampling zero air.

(c) NOx and the aforementioned components of NOz usually dominate NOy, such that any transmission of these species constitutes a sizeable measurement error for pNit. This should have been taken into account in an explicit error analysis as part of the

pNit data reduction.

(3) Aerosol nitrate can be present on mineral dust as organic nitrates or on sea salt aerosol. Do other nitrate salts convert to NO2 in this inlet?

(4) How does the instrument perform above the 1-micron size range? The latter dominates aerosol mass in many regions.

(5) Ambient air measurements of pNit:

(a) How was the error due to break-through of NOx considered?

(b) How were denuder memory effects taken into account in the reduction of the field data?

(c) The RH dependence of denuder performance is a considerable issue considering the inlet is periodically flooded with dry zero air and then re-exposed to humid ambient air. How does this back-and-forth affect the field data?

(d) How long was the inlet for the NOy channel? Was conductive tubing used (or were aerosol lost on the inlet)?

(e) Since the TD-CRDS data were not compared with an independent measurement of NOy (Mo converter CL) or of total aerosol nitrate (High-volume impactors, PILS, MARGA or similar), the claim that this instrument accurately quantifies NOy and particulate nitrate in ambient air is not substantiated and the conclusions need to be weakened accordingly.

(6) The authors show several pages on the interference due to gas-phase NH3 only to conclude it to be insignificant. However, much more NH3 is typically present in the form of aerosol ammonium, which would evaporate in the NOy inlet. The authors should also consider and examine conversion of (NH4)2SO4 especially in the presence of O3.

(7) General organization:

(a) The introduction with its lengthy discussion of nitrogen oxide chemistry misses the mark (see detailed comment below).

(b) A critical comparison of the performance of this new instrument to existing methods (in terms of detection limits, selectivity, instrument including heater designs, etc.) is lacking and should be provided.

Specific comments

pg 1 line 10 "detection" replace with quantification

pg 1 line 14 "detection limits" Please state the level of confidence. Why does the NOy channel have half of the LOD of the NOx channel?

pg 1 line 17, 18, 19 "significant interferences", "high particle transmission", "essentially complete removal" Please be quantitative.

pg 1 line 19 "denuder suffered from NOx breakthrough" Does the breakthrough of NOx not imply that the pNit measurement is inaccurate and does not work?

pg 1 line 21-22 "NOx measurements obtained from a ship sailing through the Red Sea, Indian Ocean and Arabian Gulf .... were in excellent agreement with those taken by a chemiluminescence detector of NO and NO2." What about the NOy and pNit data during this cruise?

pg 1 line 23 "A dataset exploring variations in the NOz to NOy ratio (maximum value of 0.6) of air in a region (Mainz, Germany) with strong urban influence was measured over a one-week period in winter." and what was the conclusion?

pg 2 line 1 - pg 3 line 21 Section 1.1 "Atmospheric NOx and NOy". This paper is about a new instrument. The lengthy description of NOx and NOy chemistry and all those reactions (in particular R6-R10) are not needed and could / should be replaced by citations to the authors' own papers.

If this section stays, please fix R8. RH is already used as relative humidity and implies

a saturated alkane, with which NO3 barely reacts and usually does not form an alkyl nitrate.

pg 4 line 17 "Pyrolysis". Thermolysis or thermal dissociation are more appropriate here.

pg 4 line 25. "which overcome these limitations" Please be more specific here. One of the limitations discussed in the preceding paragraph mentions secondary chemistry by O-atoms formed from the decomposition of ozone, which wasn't addressed in this paper.

Since some of the co-authors have described multi-channel TD-CRDS instruments previously (Sobanski et al., 2016; Thieser et al., 2016), please add a short statement explaining how this new instrument differs from the old ones and what parts constitutes novelty (use of a denuder to quantify pNit).

pg 5 Section 2.1 "CRDS Operation Principals" How much of this section is duplication of (Sobanski et al., 2016; Thieser et al., 2016)? Please condense and focus on what has been changed since the earlier versions, and why.

pg 5 line 5 spell out / define STD

pg 5 line 21 Please give an uncertainty for l/d.

pg 5 line 23 "aerosol particles" should simply be particles.

Does a 2 μm pore size filter truly removes all particles? In our experience, they do not, but they remove the size range that would interfere optically. Consider rephrasing.

pg 5 line 27 "depending on "flow, pressure and inlet set-up" State typical pressures and flows. Is the inlet described anywhere? Please call out the relevant section if it is.

pg 5 line 29 300 pptv NO2 equivalent and 6.5 Torr pressure difference seem like a lot. It seems to be caused by the peculiar addition point of the zero air between the valve/denuder/inlet converter and CRDS cells and probably could be avoided alto-

gether if zero air were added at the tip of the inlet (with larger fittings). Please provide a rationale why zero air was added this way (state advantages and disadvantages).

pg 6 line 9. "The maximum concentration of NO2 (and thus optimal conversion of NO to NO2)". Please state what fraction of NO that is converted and if the NO data were corrected accordingly.

pg 6 Section 2.3 How is temperature measured in these furnaces? Is the oven temperature identical to the temperature of the gas travelling through it?

sections 2.3 and 2.4. A critical parameter is the sample flow rate, which should be stated here.

pg 6 line 20. How short is "short"?

An experiment of the inlet setups during the two field campaigns should be provided.

pg 6 line 22. Describe the valve (make & size etc.). Are there memory effects? Pressure drops?

pg 7 line 11 "Results and discussion, 3.1 The fractional conversion of NOz to NO2 in the TD-inlets was investigated in a series of experiments in which constant flows of (separately) PAN, isopropyl nitrate and nitric acid were passed through the heated-inlet (bypassing the denuder) while the temperature was varied and NO2 was monitored"

This section describes how the experiment was conducted and should be moved to the experimental section, and not appear under "Results and discussion"

pg 7 line 20. $\sim$400 $^\circ$C to dissociate PAN is very high. How and where exactly is this temperature measured? What is the difference between the measured temperature and the temperature of the gas stream?

pg 7 line 22 "We conclude that PAN is stoichiometrically converted to NO2" Just because the curve has flattened does not imply stoichiometric conversion. Has this statement been verified, e.g., by comparison to a CL NOy instrument or PAN-CIMS?

pg 7 line 24 it is also higher than Day et al. (2002), Paul et al. (2010), Di Carlo et al. (2013) and Sadanaga et al. (2016) and inconsistent with CIMS inlet performance (Slusher et al., 2004; Zheng et al., 2011; Mielke and Osthoff, 2012; Phillips et al., 2013).

pg 7 sections "3.1.1. PAN" and 3.1.2 "Isopropyl nitrate". Please comment on the possibility that the PAN and iPN sources contain impurities. PAN, for instance, will slowly decompose and form nitric acid and an alkyl nitrate.

pg 7/8 "3.1.2 Isopropyl nitrate" and "3.1.3" I am skeptical about the accuracy of these thermograms. The overlap of iPN and HNO3 is inconsistent with literature.

pg 8 line 3 "expected" Expected how?

pg 8 line 20. Please also compare with Di Carlo et al. (2013).

pg 8 lines 22-25. If the temperatures are truly that inaccurate, please consider at least rough-calibrating the temperature scale.

pg 8 line 26. "Rather short" Why so short?

In such a short inlet, the gas stream is likely heated very unevenly, leading to considerable broadening of the TD profiles. Was this intentional, or is this a design flaw? Note the broadening would not explain the overlap of iPN and HNO3 thermograms.

pg 8 line 29 if this calculation can be performed for 50% conversion, it can also be done for 10%, 20%, 30%, etc. to construct an expected TD profile, which in all likelihood will be inconsistent with Figure 2.

pg 8 line 32 "to ensure complete conversion of each trace gas to NO2". Replace complete with maximum conversion.

pg 9 line 4 "verify quantitative ... conversion to NO2". Quantitative conversion was not demonstrated in this work; In fact, Figure S2 suggests incomplete conversion ($\sim$85%; or 13/15 for HNO3).

pg 9 line 6. Section "3.1.4 NH3" Womack et al. (2017) showed NH3 to be non-issue under most conditions, which is the same conclusion reached here. Does this insignificant interference really warrant two full pages? Consider condensing.

If NH3 can be converted to NOx, what happens when NH4NO3 or (NH4)2SO4 aerosol are sampled?

pg 9 line 22 "addition of 30 ppbv isoprene to zero-air did not significantly reduce the NH3-to-NO2 conversion efficiency under dry conditions, but reduced it by a factor of two when the RH was increased to 50%" In the preceding section, it was shown that NH3 converts when there is a lot of O3 present; please clarify if isoprene was added in the absence or presence of O3 (with which it would react)?

pg 11 R22. How much CH3C(O)O2NO2 are expected in a heated inlet? Its dissociation reaction is missing.

pg 11 equation (2). Is this equation valid for the likely turbulent flow conditions in the inlet?

pg 12 line 24/26 "Particle loss calculator (PCL)" Should this be PLC?

pg 12 line 26 "which was developed for cylindrical piping and not the square honeycomb shape of the denuder and also does not take into account losses due to impact at the finite surface area which the gas/particle flow is exposed to at the entrance to the honeycomb" Based on this statement, wouldn't it be reasonable to conclude that this calculator should not be used?

pg 13 line 6. "close to 100%". Please provide a table with the precise values and some statistics.

"humidified significant" Grammar.

"RH-dependent breakthrough". During zeroing, dry air is added and some of it travels through the denuder; does the denuder require some conditioning then after the switch

back to ambient air sampling?

pg 13 line 9. "≥95%. Please give precise values. Since NOx is usually the major component of NOy, the partial and variable (as a function of RH) transmission of NOx introduces a major bias when quantifying aerosol nitrate.

pg 13 line 12. Why dry nitrogen (if the behaviour is different at high RH)? Is this really equivalent to 1 month of sampling ambient air? How was 2.30ïĆť1017 molecules derived at?

pg 13 line 20 "2.55x1015" what are the units here?

pg 13 line 23 "After loading the denuder with 5 sccm from a 0.831 ppm NO2 gas bottle for 4.8 days" NO2 cylinders usually co-emit HONO, HNO3 and NO. Was this considered?

pg 13 line 24 "(a total of 7.60 x 1017 molecules deposited)" How this value determined?

pg 15 line 14 sections 4.1 and 4.2 are not convincing since there is no independent measure of what to expect for pNit.

pg 16 line 10 Does the AMS quantify supermicron particles at all? A citation is needed.

pg 17 line 18 "> 90% transmission for ammonium nitrate". Is this statement justified when the transmission varies with size as shown in Figure 5?

pg 21 line 45. The accepted paper should be cited.

pg 22 line 28. The accepted paper should be cited.

pg 23 line 13 The paper by Womack et al. (2017) has been accepted and should be cited and not its discussion paper.

pg 24 Figure 1. Please add more detail such as dimensions; for example, indicate the diameter of the critical orifice and air pressure, and show l and d.

Figure 1 shows that ambient air is drawn in through two valves ("V")? Are these de-

scribed anywhere? How much of a pressure drop do they give? What is the internal surface made of (Teflon?)?

In Figure 1, "1/2 in PFA" should be in metric units; indicate if this is outer or inner diameter and how long this section is.

In Figure 1, what does the green line represent? A chamber wall?

The Figure is inconsistent with the text as it shows a TD oven at 850 °C which is roughly the same length as the denuder; in the text, the section actually heated is described as rather short or 3 cm long, and the denuder length is stated at 10 cm.

pg 25 Figure 2. The PAN and iPN thermograms are inconsistent with literature. The caption should state the level of O3 present for the NH3 experiment.

pg 26 Figure 3 is not essential to this paper and probably should be in the supplemental.

pg 28 Figure 5. Please specify the type of aerosol diameter (geometric vs. mobility). State value of key parameters (flow rate, denuder diameter). Correct inconsistency between PLC and PCL.

pg 29 Figure 6. Please zoom in to ~60% to 100% for NO and to 95% to 100% for the other gases. Often, NO and NO2 are the largest components of NOy. How accurate is the measurement of NOz species if ~5% of NO2 and ~35% of NO break through the denuder? How variable are the numbers shown in Figure 6 (add error bars)?

pg 30 Figures 7. What do the blue shades represent and why does the RH change (state in caption). As stated in the comments above, I am not convinced this experiment provides relevant information for an ambient air measurement (conc. are simply too high).

pg 31 The presentation of Figure 8 is unclear. How this experiment conducted? Is synthetic air equal to zero air (and why is it humid then)? In panel (a), why is there

a "bump" at 9:50? In panel (b), what does the derivative mean to the reader? What time? Why are there lines for different RH?

pg 32 Figure 9. Properly cite Kim et al. in the bibliography, and do not provide the full reference in the caption.

pg 33 Figure 10a. Is the slope correct? There seem to be many points above the line. Is the slope affected by outliers? In any case, it's great that NOx data agree, but since the focus of this paper is mainly on measurement of NOy, NOz and particle nitrate, a more relevant plot would be TD-CRDS NOy vs. CLD NOy, TD-CRDS NOz vs. NOz measured by other techniques, as well TD-CRDS nitrate vs PILS or MARGA nitrate.

pg 33 Figure 10b I am not sure the OPC data add anything of value here since the nitrate fraction could be changing.

Supplemental:

Figure S1. Please provide the mechanism used in the box model.

Figure S2, caption. "total uncertainty of the TD-CRDS measurements" - what is meant by this?

Figure S2D is inconsistent with Figure 2 which shows the entire TD profile of iPN overlapping with that of HNO3 - which is not observed in Figure S2D under any condition.

Figure S3. A strange and confusing way to present data.

The simulations consider oxidation of NO2 by O3 to form NO3 and subsequent formation of N2O5. Were NO3 and N2O5 sinks been considered? Please provide the full mechanism.

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