Reply to Anonymous Referee #2

In the following, the referee's comments are reproduced (black) along with our replies (blue) and changes made to the text (red) in the revised manuscript. Line numbers are referring to the unrevised version of the manuscript.

Dewald et al. examined the conversion of isoprene derived nitrates to NO2 in heated inlets. The isoprene nitrates were generated from reaction of the nitrate radical with isoprene in a large environmental chamber. Three inlet designs were evaluated: a conventional heated quartz tube, common in such instruments, a quartz inlet containing glass beads, and a heated inlet constructed from PFA Teflon. Measurement artifacts arising from the thermal decomposition of ozone (to atomic oxygen) and of nitric and nitrous acid (to hydroxyl radical) were evaluated.
This is a well-written and thorough manuscript. The paper will be of interest to the growing community of TD-CRDS and TD-CEAS users and within the scope of AMT. I recommend publications once the authors have considered my comments below.
We thank the referee for the positive evaluation of our manuscript and for the useful comments.

General comment

The abstract boldly promises a viable solution to broadened thermograms observed in the measurement of isoprene nitrates by TD-CRDS but in the end falls somewhat short of this goal. The proposed solution, a better-performing PFA inlet, is not a viable alternative to current inlet designs since it cannot be heated above ~ 500 K without melting. Perhaps more discussion is needed to better articulate what specific problem this paper ultimately has addressed.
The referee is right, this work presents a pragmatic approach to enable separate detection of PNs and isoprene-derived ANs, but not to suppress broadened thermograms under field conditions. We thus replaced the sentence in L15/16 of the abstract with:
The use of a TDI consisting of a non-reactive material suppresses the conversion of isoprene-derived ANs at 473 K, thus allowing selective detection of PNs. The potential for interference by the thermolysis of nitric acid (HNO_3), nitrous acid (HONO) and O_3 is assessed.

Specific comments

line 1/title: Replace "detection" with "quantification".
Correction made.

lines 15/16. An abstract for a scientific paper should be sufficiently representative of the paper if read as a standalone document. In this spirit, please name the "viable solution to this problem" rather than teasing the reader at this point.
We agree to that and modified the abstract accordingly (see answer to general comment above).

line 108. "by passing a fraction of the air" Is UV transparent material such as quartz used here? Please provide more experimental details.
The air was passed through a cuvette (~ 70 cm^3) that is transparent for UV light. We added this information in L108:
O_3 (up to 600 ppbv) was generated by passing a fraction of the air flowing into the chamber through a UV-transparent cuvette (~ 70 cm^3) illuminated by a low-pressure Hg-lamp (PenRay) that dissociated O_2 (to O atoms and thus O_3) at 185 nm.

lines 141/143. The temperatures required for full conversion of PN or AN depend on residence time and on where the temperatures are measured and thus are not universal. Please note the dependence of these conversion temperatures on inlet residence time(s) here (they are given on lines 176-177) and add a qualifier such as "In our inlets, ..."
line 142, 143 "results in conversion" and "additional conversion". Should this say: complete conversion?
We agree and underline these two points (non-universality of our conversion temperatures, extent of conversion) by modifying the sentence in L141-143:
At the given conditions (i.e. flow rate, pressure, residence time in the heated section), keeping our TDI at temperatures close to 448 K, results in quantitative conversion of PNs to NO_2 so that the cavity sampling via this inlet measures the sum of PNs + NO_2. Heating our second TDI to ≈ 650 K results in the complete conversion of ANs to NO_2 so that the sum of ANs + PNs + NO_2 can be measured as described in the literature cited in the introduction.

line 162-177. Please comment on (any) pressure drops associated with placing glass beads in the inlet.

The presence of glass beads in TDI-1 leads to a pressure drop of ≈ 23 hPa compared to TDI-1 lacking glass beads. We add this in L166:

The glass beads were supported on a 2 cm thick glass frit and reduce the pressure downstream by ≈ 28 hPa compared to TDI-1.

line 166. Wouldn't the glass bead also lead to more uniform heating of the sampled gas and thus aid in the dissociation of PN and AN?

This is indeed what we would expect and partially explains why TDI-2 produces thermograms of iPN similar to that obtained with TDI-1 despite their different heating section lengths. We already mention this in L221.

line 180/Figure 2. Please state the temperature of the SCHARK chamber. Assuming it is 298K, one would expect with ~4 ppbv of NO2 an equilibrium N2O5:NO3 ratio of ~3:1, as was indeed observed at 11:45. However, the observed ratios at the earlier times (e.g., at 10:45) seem lower than expected from equilibrium. Under the conditions described here, the time to achieve equilibrium should be sufficiently short (minutes). Please comment as to why the N2O5:NO3 deviates initially.

The temperature of the SCHARK was not recorded, but is close to room temperature (296 ± 2 K). The observed change in the N_2O_5:NO_3 ratio in the above-mentioned period (when the chamber was not in steady-state yet) is entirely consistent with an increase in the NO_2 concentration from 3.4 ppbv (at 10:45 LT) to 4.8 ppbv (at 11:45).

line 186 "after subtraction of the N2O5 mixing ratios" - please indicate that you are subtracting N2O5 here in the figure legend and caption and note that you are also subtracting NO2 (I am guessing).

Correct, both NO_2 and N_2O_5 were subtracted from the signal obtained with the TDI-channels. We add this information in the caption of Fig. 2:

Note that the NO_2 and N_2O_5 mixing ratios were subtracted from the organic nitrate signals (middle panel).

line 187 The residual signal is curious. Is it possible NO2 is lost in the low-temperature reference channel to NO2+O3 and N2O5 formation but not in the heated channel?

Given the short residence time in the unheated inlet (0.33 s) and the low rate coefficient of the reaction between O_3 and NO_2 at 298 K (3.5×10^{-17} cm^3 $molecule^{-1}s^{-1}$; IUPAC, 2021) only ≈ 0.1 pptv of 4000 pptv NO_2 would be converted to NO_3 in the presence of 100 ppbv O_3. We thus keep the alternative explanation for the residual signal in L187.

line 194-195. Since the amount of isoprene added (i.e., its concentration) is known (line 202), please calculate the yield of AN relative to integrated amount of NO3+Isoprene.

The concentration of isoprene in flow steady-state in the presence of all reactants was not measured but calculated from the flows and expected consumption by O_3, NO_3 and OH. In addition, the chamber is not characterised for wall loss of ISOP-NIT and due to the long residence in the chamber in combination with the high amounts of O_3, ozonolysis of ISOP-NIT may bias the AN yield determination additionally. For that reason, any AN yield estimated from this would be highly speculative. The sentence in L202 concerning the isoprene concentration is misleading though. To clarify that isoprene concentrations after oxidation are not measured, we modify the sentence in L202:

This is however never the case in the present experiments as isoprene is continuously flowed into the chamber and remains according to model calculations (see below) at a level of ≈ 11.4 ppbv.

line 200 "Very low concentrations" Please be quantitative.

The concentration of isoprene has to be low and the concentration of e.g. aldehydes (or other precursors) high enough so that the reaction of NO_3 towards (usually less reactive) aldehydes becomes competitive to the one with isoprene. The threshold concentration is thus highly dependent on the experimental conditions (i.e. yield of precursors vs. steady-state concentration of isoprene) and not universal. Instead of giving a concentration, we rephrase the sentence in L200:

The formation of PNs only takes place once isoprene has been depleted so that secondary oxidation of the above-mentioned aldehydes by OH or NO_3 leading to further acyl-peroxy radicals (which form PNs) become at least competitive to the primary oxidation of isoprene.

line 201. Consider adding a reaction scheme for clarity.

Considering the minor importance of the very limited routes for PN formation in the dark we prefer not to add a reaction scheme which would distract from the reaction paths we list that are relevant for this work.

line 205-206. "This reaction path is a minor one" How do you know this?

The branching ratios given in Nguyen et al. (2016) imply that the acetyl peroxy radical is formed with a relatively low yield, which is consolidated by the CIMS measurement in Fig. 12. We modify the sentence in L205:

However, according to the branching ratios given in Nguyen et al. (2016), this reaction path is a minor one and $CH_3C(O)O_2$ (and thus PAN) should be formed in negligible amounts.

line 258. Please describe the Iodide-CIMS and how it "was coupled to the experiment" in section 2 "Experimental".
We added a brief description of the CIMS instrument and given the minor importance of the CIMS measurements to this work, we prefer to append it as section S8 in the Supplement rather than in the “Experimental section:

S8 Detection of PAN, HONO and HNO_3 with I-CIMS
A chemical ionization mass spectrometer using iodide primary ions (I-CIMS) described recently (Dörich et al., 2021) was deployed to detect PAN, HONO and HNO_3. The I-CIMS was coupled to the SCHARK via ≈ 2m of ¼ inch PFA tubing heated to 40 °C. The flow rate through the PFA-tubing was ~2.1 SLM. Iodide anions were generated by passing 4 sccm of 400 ppmv methyl iodide (CH_3I in N_2) diluted in 750 sccm N_2 (Westfalen, 5.0) through a 370 MBq polonium (^{210}Po) source. PAN was thermally dissociated in an heated inlet (PFA tube at 170°C, residence time of 40 ms) to peroxy acetyl radicals which are detected as acetate ions $CH_3CO_2^-$ (*m/z* 59) after reaction with I^- (Phillips et al., 2013). Calibration was performed using a photochemical PAN source (Warneck and Zerbach, 1992). HNO_3 was detected as the $I^-(HNO_3)$ cluster ion at *m/z* 190 and calibrated using an HNO_3 permeation source characterised by optical absorption. HONO was detected as NO_2^- (*m/z* 46) using acetate anions (Veres et al., 2008) generated by adding a high concentration of PAN to the TD-inlet.
We refer to this in the main text in L258-260:
In order to identify the trace-gas(es) responsible for the signals observed in the system without isoprene, an Iodide-Chemical-Ionization Mass Spectrometer (I-CIMS (Eger et al., 2019)) described in the Supplement (S8) was coupled to the experiment.

Line 267. How was the mixing ratio of 22 ppbv HNO3 determined?
The HNO_3 mixing ratio was calculated from the permeation rate and flow rates. We added the following text to L267:
In these experiments, 22 ppbv HNO_3 with 780 pptv NO_2 impurity in dry synthetic air was delivered to the TDIs along with 350 ppbv O_3. The HNO_3 mixing ratio was derived using a known permeation rate (Friedrich et al. 2021) and dilution factor.

Line 279 "by the scavenging of O-atoms". While this is plausible explanation, please note the speculative nature of this statement. Rather than scavenging O atoms, the surface could act to catalyze 2O->O2, for instance.
We agree and modify this sentence in L279:
In TDI-1 this is prevented by the removal of O-atoms by the glass beads (e.g. via scavenging or surface-catalysed recombination to O_2).

line 288. "H2O drives HNO3 from the surface and thus protects it from surface reactions". How much water would you expect to be sorbed to surfaces in an inlet heated well above the boiling point of water?
At high temperatures, the physi-adsorption of water is of course greatly reduced but not zero. One must bear in mind, that the concentration of H_2O relative to HNO_3 is very large and competitive adsorption will play a role in determining the surface adsorption (and thus further reactions) of HNO_3.

line 350-351. The instrument must have sampled a very large concentration of nitric acid for a long time to produce such a large artifact.
Correct, but especially the example shown in Fig. S4 was measured before we were aware of that problem and after the unheated TDI sampled air from the SCHARK containing residual HNO_3 and ISOP-NIT for several hours. Given the fact that keeping the TDI below 400 K for ca. 30 minutes while sampling ca. 2.8 ppbv ISOP-NIT (and probably HNO_3) is sufficient to create a peak signal of ca. 10 ppbv when heating back to 703 K (see Fig. S5), this appears plausible.

line 400. Replace Torr with SI units, please.
Correction made, instead of Torr we now use hPa. The same was done in L138 and L176.

line 423. Please move the experimental details to the experimental section.
We are aware of the fact that it is unconventional to provide experimental details in the results section. But since this is a special modification of the setup that is only relevant in this paragraph, we are convinced that it is easier to follow the manuscript, if the details are kept at this place.

References

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