Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., referee comment RC2
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Comment on amt-2021-128

Anonymous Referee #2

Referee comment on "Impact of ozone and inlet design on the quantification of isoprene-derived organic nitrates by thermal dissociation cavity ring-down spectroscopy (TD-CRDS)" by Patrick Dewald et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-128-RC2, 2021

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.

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.

Specific comments

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

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.

line 108. "by passing a fraction of the air" Is UV transparent material such as quartz used here? Please provide more experimental details.

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?

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

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?

line 180/Figure 2. Please state the temperature of the SCHARK chamber. Assuming it is 298K, one would expect with ~4 ppbv of NO_2 an equilibrium N_2O_5:NO_3 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 N_2O_5:NO_3 deviates initially.

line 186 "after subtraction of the N_2O_5 mixing ratios" - please indicate that you are subtracting N_2O_5 here in the figure legend and caption and note that you are also subtracting NO_2 (I am guessing).

line 187 The residual signal is curious. Is it possible NO_2 is lost in the low-temperature reference channel to NO_2+O_3 and N_2O_5 formation but not in the heated channel?

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 NO_3+Isoprene.

line 200 "Very low concentrations" Please be quantitative.

line 201. Consider adding a reaction scheme for clarity.

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

line 258. Please describe the Iodide-CIMS and how it "was coupled to the experiment" in section 2 "Experimental".

Line 267. How was the mixing ratio of 22 ppbv HNO_3 determined?

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 $2O \rightarrow O_2$, for instance.

line 288. "H_2O drives HNO_3 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?

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.

line 400. Replace Torr with SI units, please.

line 423. Please move the experimental details to the experimental section.