

Atmos. Meas. Tech. Discuss., referee comment RC1
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Comment on amt-2020-520

Anonymous Referee #1

Referee comment on "Thermal dissociation cavity-enhanced absorption spectrometer for measuring NO₂, RO₂NO₂, and RONO₂ in the atmosphere" by Chunmeng Li et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2020-520-RC1>, 2021

The authors report on a new dissociation cavity enhanced absorption spectrometer for quantification of NO₂, RO₂NO₂ and RONO₂ in the atmosphere. The instrument relies on cavity-enhanced absorption spectroscopy to quantify NO₂ and NO₂ generated from organic nitrates by sampling through a heated inlet similar to what has been described by others (Thieser et al., 2016; Paul et al., 2009; Keehan et al., 2020; Chen et al., 2017; Wooldridge et al., 2010; Sadanaga et al., 2016; Di Carlo et al., 2013). Inlet characterization and sample field data are presented.

Overall, this is a well written manuscript suitable for publication for AMT after my comments below have been addressed by the authors.

Major comments

- Considering the large body of existing TD literature, a table comparing this new instrument to existing methods and a discussion of the differences, advantages and disadvantages should be added to the paper.

Specific comments

Title - replace 'detecting' with 'measuring' or 'quantification of' (the instrument does not merely detect the presence of PN and AN after all).

line 102. Since the instrument samples through a PTFE filter, the Mie scattering component should be zero.

line 110. Please comment on the precision of the output power of the stabilized source.

line 119. reported by whom? ATF?

line 155 please state the manufacturer and internal surface of the T-shaped solenoid valves.

line 160. Hg lamps tend to "run hot" which can affect the output of PAN, which is prone to thermal dissociation. Has the composition and purity of the PAN source been evaluated? Furthermore, what was the concentration or mixing ratio of acetone used?

line 166 which requirements?

line 182. Please describe how N₂ and He were delivered (sampled from the tip of the inlet, or statically).

line 226. Please justify omitting glyoxal from the fit and estimate the uncertainty introduced. Figure 4 suggests that the contribution of glyoxal was small but that may not always be the case. What (if anything) happens to the NO₂ retrieval when glyoxal is included in the fit?

line 236 - Figure 4. Please state the uncertainty of the NO₂ mixing ratios (16.2±? ppbv).

line 240 - Figure 5. It seems that the timing of the inlet temperature switch was off as there are blue data points at the same level as [NO₂]_{ambient} and red data points at the same level as 180 °C.

line 248 It is 1 spectrum, but the plural should be 2 spectra (not "spectrums").

line 283. An alternative (and more likely) interpretation of the second plateau is the presence of alkyl nitrate impurity. What are the operating temperature and the output purity of the photochemical PAN source? Is $[\text{PAN}]_{\text{out}} = [\text{NO}_x]_{\text{in}}$?

lines 283-284. The PAN dissociation temperature of 400 °C reported by Friedrich et al. is an outlier and inconsistent with every other paper on this subject. At a residence time of 142 ms (line 153) and using rate constant for unimolecular decomposition reported by (Kabir et al., 2014), PAN is predicted to be 99% dissociated at a temperature of "only" 127 °C.

line 286 - how much time is there for recombination to occur?

line 290. $\text{CH}_3\text{O}_2\text{NO}_2$ more readily dissociates than PAN; under the conditions of the authors' inlet, it is predicted to be >99% dissociated at a temperature of <50 °C.

line 291. The two plateaus can also be interpreted as a ~2:1 mixture of PAN and alkyl nitrates - can this be ruled out (see question for lines 160 and 283).

line 294. Please state how much time there is for recombination to occur.

line 318 Caption to Figure 7 - are gray/green and PAN/ NO_2 backwards?

line 326 Filter and wall losses are small only if they the filter and wall material are made from Teflon. Please rephrase.

The statement is true for ANs such as methyl or ethyl nitrate; not sure the statement is true for isoprene nitrates that are prone to hydrolysis (Vasquez et al., 2020).

line 426 Replace MeN with Methyl nitrate (one is not supposed to start a sentence with an abbreviation or acronym).

line 448. It is worthwhile noting that these molecules are important only at night and early morning hours - for this reason, the Cohen group has generally not reported AN data at those times of day.

Please cite (Thaler et al., 2011) for ClNO₂ and (Womack et al., 2017) for N₂O₅.

line 462/465. It is 1 spectrum, and 2 spectra (not "spectrums").

line 465 "as shown in Fig. 9a. The 21077 spectrums" Figure 9a does not show this information (11a perhaps?). What is meant by 21077?

line 467 Fig. 9b should be 11b.

line 500 "up to 0.99" - please state the actual value of r

line 514 Figure 13. I am not sure what is plotted here. The GC-ECD data are labeled "PAN" on the left-hand side, but PNs on the right-hand side. The TD-CEAS data are labeled PNs on the left but PAN on the right.

In principle, the GC-ECD can observe PAN, PPN etc. and those can be summed to ΣPN. Was this done?

Literature cited

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