Atmospheric Measurement Techniques Discussions

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Comment on amt-2020-520

Anonymous Referee #2

Referee comment on "Thermal dissociation cavity-enhanced absorption spectrometer for measuring NO_2, RO_2NO_2, and $RONO_2$ in the atmosphere" by Chunmeng Li et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2020-520-RC2, 2021

Summary: The authors present a new thermal dissociation cavity enhanced absorption spectrometer (TD-CEAS) for measurement of NO_2, peroxy nitrates (PNs), and alkyl nitrates (ANs). They demonstrate, through lab tests and box model simulations, that interferences can be corrected for, and that the instrument outputs accurate measurements when compared to a chemiluminescence detector. Finally, results from a measurement campaign in Chengdu, China are presented, demonstrating its effectiveness in ambient conditions.

In general, this manuscript successfully demonstrates the performance of this new instrument, carefully considering the difficulties in converting PNs and ANs to NO_2 in a thermal dissociation oven. There are some significant grammatical/English errors throughout the manuscript, which in some cases make the details difficult to understand but these can be fixed. I would recommend publication, after the authors address some comments below, as well as editing the English.

General comments:

The authors sometimes refer to the ANs channel, and sometimes to ONs channel, which is confusing. This should be made clear throughout the manuscript that these are different, but related to each other.

Section 3.4 demonstrates that the 180 degree oven is not sufficiently hot enough to prevent recombination of PA and NO2, with efficiencies ranging from 0.5 to 0.9 at 180 degrees. Are the authors correcting for this incomplete thermal dissociation in the rest of the paper? If so, this should be stated clearly. If not, this seems like a *major* inaccuracy of

the measurement and should be addressed. Figure 9 makes it look like it isn't being made, since the intercept at x = 0 doesn't match what the legend says the input PAN concentration is.

The authors should more clearly demonstrate how they convert the measured α(λ) to [NO2]. Perhaps another equation would be helpful here in section 3.3, demonstrating that it is a linear fit of all the possible gas-phase absorbers in that wavelength region.

As the authors state on line 533, sudden changes in the ambient NO2 while this instrument is measuring from the PNs and ANs would pose a significant problem. Probably this instrument is only useful when a simultaneous measurement of NO2 is available. Most field campaigns do have NO2 measurements, so this likely isn't a major issue, but the authors should address it anyway.

Many of the references have titles listed in all capital letters, which should be changed.

Specific comments:

Line 32: "One is peroxy acyl nitrates (PANs)…". The other one is never defined. Is it the peroxy nitrates without an acyl group, as mentioned in line 34?

Line 33: Define PAN here, to differentiate from the more general PANs.

Line 46: "with a small branch ratio (1% - 30%)": Which reaction (R3a or R3b) is defined as the one with the 1 – 30% branching ratio, and which is the 70 – 99% reaction?

Line 75: "the importance of PNs and ANs in regulating ozone formation has not been well studied [in China]": The absence of citations here implies it has not been studied at all, which is not true. Examples include: Liu 2010, Zhang 2014, and Liu 2018. Some citations should be included here.

Line 92: Fig S1 only shows the wavelength range 430 – 460 nm, so this line should be changed to match.

Line 151: "… for the ANs and PNs channels are controlled at 180 degrees and 380 degrees, respectively". These numbers appear to be backwards, as the ANs channel was at 380, not 180 degrees.

Line 154: Presumably the solenoid valves are made of stainless steel? Do the authors expect any NO2 losses on this steel?

Line 175: Define the MCM, and include a citation.

Line 229: "The corresponding fitting residual is in the range of 10 x 10^-9, suggesting the system can guarantee the accuracy…". What is the meaning of this number and why does it imply the system's accuracy? Wouldn't it be better to compare the residuals between the two different fits to demonstrate they are similar in their magnitude?

Line 247: Move the "CONC" label to after "One is the differential concentration method" on line 245.

Line 245 – 255: In general, this paragraph is more confusing than it needs to be. You can simply state that there are two methods, one which calculates [NO2] in each channel from equation (1) using N2 as I0, then subtracts [NO2]_ambient to yield [ANs] and [PNs]. The other method uses I_ambient as I0 to first derive a corrected α(λ), and then uses this to calculate [PNs] and [ANs]. I do not think that equations 3 – 8 are necessary.

Line 254 and elsewhere: The "SPEC" method is often misspelled as "SEPC".

Line 271 – 274: This is helpful information about why two different oven setpoints will yield PNs and ANs separately. It should be moved to earlier in the manuscript, perhaps in the introduction.

Lines 282: "platform" should be replaced with "plateau".

Line 345: These interferences of a few percent, while not large, are still non-negligible. Are the measurements being corrected for these interferences? If so, that should be stated clearly.

Line 366: "as described above" should be "as described below"

Line 367: To stay consistent with previous sentence, replace “RO2” with “PA”

Lines 426 – 441 and equations 9 – 12: This is another example of a paragraph that is much more confusing than it needs to be. It seems that you could just say that to accurately measure ANs, you must first measure PNs in the 180 degree channel, apply a corrective factor based on the first look-up table, then subtract this from the raw ANs channel, then apply a second corrective factor based on the second look-up table. The way the authors have written it, with many new parameters such as [PNs_C] is just more confusing.

Line 472: “… the interference in the heated channels, which should be larger than 8%”. Where does this number come from?

Line 484 – 487: This is repeating how the corrections are made, and was already stated in the previous section, so it doesn’t need to be repeated here. Doing so implies that the technique is different here.

Line 535 – 538: These lines are introducing new information to the analysis, and should be included in the results and discussion section instead of the conclusions section.

Figure 2: Zoom in on the left-hand axis which shows reflectivity. It is difficult to see the full range of R.

Figure 3: Why do the authors expect the d_eff / L vs flow rate plot to be linear? A linear fit implies that at the intercept, where flow rate = 0, then d_eff / L will be 0.79, when in fact, d_eff / L should approach 0 as the flow rate decreases to 0. On the other end, as the flow rate gets larger, the d_eff / L will get larger, but will never get to 1 or higher, as a linear fit would imply. It seems that an exponential fit (d_eff / L = A – Be^(C*flow_rate)) would be more appropriate.

Figure 7: The caption states that the orange columns correspond to HNO3, but the legend indicates CH3O2NO2. Which is correct?

Figure S5: How was this simulated? Was it checked experimentally? How do the authors reconcile this non-uniform temperature profile with their statement on line 152 that “it is assumed that the temperature of the heating part is uniform”?

Figure 9: The y-axis label is confusing. Doesn't using the SPEC method mean that the resulting [NO2] is simply [PN], without needing to subtract [NO2]_ref?

References

- Liu et al, Evidence of reactive aromatics as a major source of peroxy acetyl nitrate over China, ES&T 44, 7017 (2010)
- Zhang et al, Wintertime peroxyactyl nitrate (PAN) in the megacity of Beijing: Role of photochemical and meteorological processes, J. Environ. Sci, 26, 83 (2014)
- Liu et al, Understanding unusually high levels of peroxyacetyl nitrate (PAN) in winter in Urban Jinan, China, J. Environ. Sci. 71, 249 (2018)