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Atmospheric Measurement Techniques Discussions

Interactive comment on "Aircraft based four-channel thermal dissociation laser induced fluorescence instrument for simultaneous measurements of NO_2, total peroxy nitrate, total alkyl nitrate, and HNO_3" *by* P. Di Carlo et al.

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We thank Referee 2 for the careful attention to this manuscript providing us appreciated comments that have improved the manuscript. Below we have included the review comments followed by our responses in italics. In the revision of this manuscript, we will highlight those changes accordingly.

Di Carlo and collaborators describe a recently constructed 4-channel thermal

dissociation laser induced fluorescence instrument for aircraft measurements of NO2, ΣPN, ΣAN, and HNO3. The instrument design is based on a similar Berkeley instrument previously described by Day et al. (2002) which has been validated on several occasions (e.g., Wooldridge et al., 2010). The manuscript is well written and I personally found it an interesting read. Overall, I found that the manuscript itself does not contain anything dramatically novel; however, I suppose that it can still be relevant and of interest to this journal's audience. I therefore favor publication, but would ask for inclusion of more ambient measurements and their discussion prior to publication to strengthen the paper and my comments below to be addressed.

Response:

We thank the Reviewer for the suggestion, however the aim of this paper was to focus on the experimental and technical aspects of the developed instrument, so we believe that the ambient measurements reported are enough to prove the system performance, more ambient measurements are going be presented in near future publications.

General comments

1) While the NO2, ΣPN, and ΣAN measurements are validated, there is no validation of the HNO3 measurement, which of the four species is the most challenging to measure accurately.

Response:

We have not had the chance to validate the HNO3 measurements in a field campaign so far, but the laboratory tests reported in this paper show that the system is able to detect HNO3, and isolate its concentrations, from that of other NOy compounds.

2) Throughout the manuscript, the authors use the acronyms PN and AN, but ΣPN and ΣAN are also used. I am not sure if there is a distinction between these two I am missing, but it seems to me that they are one and the same. If so, please either

correct or clarify. Also, since the authors consider N2O5 as part ΣPN (Figure 10), please include NO3 and N2O5 in its definition (page 8762, line 2).

Response:

We used AN and PN when we talked about a single peroxy nitrate or a single alkyl nitrate (as defined at page 8762, line 15), while when we talked about the total peroxy nitrates or total alkyl nitrates we used ΣPNs and ΣANs, as defined at page 8763, line 20. In the abstract (page 8761, line 23) and at page 8773, line 27, is stated that ΣPN includes N2O5.

3) Please comment (in the manuscript) on whether any of the instrument channels is sensitive to interference from aerosol nitrate (either organic or inorganic).

Response:

This is a good point, we have added a comment on this issue (page 8768, line 11) as: "The heated cells dissociate all the gas phase nitrates, but also any aerosol phase (nitrates Day et al., 2002)".

4) Please state figures of merit of this instrument (detection limits, weight, power consumption, dynamic range, accuracy, precision, etc.) in an appropriate section of the paper (some of this information is currently buried in a section labeled "data retrieval and calibration").

Response:

Yes, all these pieces of information are reported in the "data retrieval and calibration" section, it is still missing the weight and power consumption that we are going to add in the revised version after the description of the rack system (page 8765, line 13) as: "The TD-LIF system, including the FAAM rack, weighs 224 kg and the power consumption is less than 1.5 kW"

5) I agree with the first reviewer that several key papers in this area have not been cited, for example: Wooldridge, P. J., et al. (2010), Total Peroxy Nitrates (SPNs)

in the atmosphere: the Thermal Dissociation-Laser Induced Fluorescence (TD-LIF) technique and comparisons to speciated PAN measurements, Atmos. Meas. Tech., 3(3), 593-607. Fuchs, H., et al. (2012), Comparison of N2O5 mixing ratios during NO3Comp 2007 in SAPHIR, Atmos. Meas. Tech., 5(11), 2763-2777.

Response:

We thank the Reviewer for this recommendation, we have added the suggested papers in the reference list and those suggested by the first Reviewer, including the following integrations through the paper: 1) "Recently it has been showed that, at a temperature sufficient to thermally dissociate ΣANs into NO2, also Nitryl chloride (ClNO2) can be dissociated into NO2 (Osthoff et al., 2008; Thaler et al., 2011). This species represents another NOx reservoir in the troposphere, especially during nighttime when ΣANs can also include ClNO2." (page 8763, line 22); 2) "The TD-LIF technique has been validated via intercomparison exercises with instruments using different detection techniques like CIMS (Beaver et al., 2012) or with instruments that measure single PANs species (Wooldridge et al., 2010)." (page 8764, line 4); 3) "In the NO3Comp 2007 intercomparison exercise, carried out in the SAPHIR chamber, was proved that three cavity ring-down instruments and two LIF instruments detect N2O5 with good agreement (Fuchs, et al., 2012); here we have reported the intercomparison in troposphere onboard the BAE 146-301 aircraft." (page 8774, line 3); 4) "Field campaigns and chamber experiments have shown that the oxidation of isoprene, the most emitted biogenic VOC, generates nitrates that can be the main fraction of alkyl nitrates, at least in sites dominated by natural emission of VOC. (Chen et al., 1998;Beaver et al., 2012). Model simulations have shown that uncertainties in the amount of nitrates produced by isoprene oxidation can impact ozone production by about 10% in the Southeastern United States (Xie et al., 2012)." (page 8762, line 24).

Specific comments

page 8763, line 14. This new approach has not just been proposed, but demonstrated on numerous occasions. Please rephrase.

Response:
This sentence will be rewritten as follow: "In the last decade a new approach has been tested and used in several field campaigns"

page 8766 - Sampling and inlet system. Please specify whether the instrument is operated with an inlet or not, and briefly discuss any potential artifacts arising from aerosol nitrates.
Response:
As wrote at the beginning of this paragraph, the system uses a common rear-face inlet. Aerosol nitrates can be thermally dissociated with gas phase nitrates, therefore in the total nitrates measured they can contribute (Day et al., 2002). The aerosol fraction can be removed with teflon filters (Paul et al., 2009), whereas a carbon denuder has been used to remove the gas fraction of ANs and detect the aerosols fraction (Rollins et al., 2010)". We will include the following sentence at page 8767, line 11: "Aerosol nitrates can be thermally dissociated like gas phase nitrates, therefore they can contribute in the measured total nitrates (Day et al., 2002)."

page 8766, lines 21-22. It is my recollection that photochemical PAN sources do not work well with thermal dissociation methods due to the relatively high acetone content. Has the output of the photochemical PAN source been verified using a method other than TD-LIF? At the minimum, a comment on the performance of the photochemical PAN source is warranted.
Response:
It is correct, acetone may be a problem for the TD-LIF, as well as for the column of the GC system. However our source of PAN is a custom system developed to drastically reduce the amount of acetone needed, as in Flocke et al. 2005. Therefore we got a quite stable PAN source for enough time to carry out the tests. The source was not checked using other methods, besides concentrations estimation from their dilution and flow, but we are confident of its reliability since we made several checks

to exclude interferences or artifacts.

Page 8770 - 8771. Consider condensing this paragraph.
Response:
We think that a detailed description of these experiments is helpful to understand what we did and how the system was checked for selectivity and interferences."

page 8772-73. It is mentioned that the instrument flew on 25 occasions, but the comparison is only shown for short segments (3 hours in Figure 9 and a 100 min segment in Figure 10). Can you comment on how the rest of the data compared? As I said earlier, inclusion (and discussion) of more of the flight data would, in my opinion, strengthen the paper sufficiently to warrant publication.
Response:
As mentioned here, we have reported some examples, just because all the other flights showed a similar behavior in terms of comparison of the TD-LIF with other instruments, with nothing interesting to show. However a detailed analysis of the data collected during the campaigns carried out so far, will be presented in the forthcoming papers.

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 8759, 2012.