

Interactive comment on “Aircraft based four-channel thermal dissociation laser induced fluorescence instrument for simultaneous measurements of NO₂, total peroxy nitrate, total alkyl nitrate, and HNO₃” by P. Di Carlo et al.

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Received and published: 18 February 2013

We thank Referee 3 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.

General comments:

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This paper presents a description of a thermal dissociation – laser induced fluorescence instrument for simultaneous, fast response measurements of 4 reactive nitrogen classes, NO₂, peroxy acetyl nitrates (PN), alkyl nitrates (AN) and nitric acid (HNO₃). The instrument is based on proven techniques that have been developed in other research groups. However, the authors have demonstrated several experimental improvements, including the use of a single, high power laser and its introduction to four LIF cells placed parallel with respect to the flow but in series with respect to the input light beam. Furthermore, the instrument has been deployed for regular aircraft use, and has been compared to in flight data from other instruments. The comparison of the PN measurement to the N₂O₅ has not been previously reported to my knowledge. Therefore, the paper certainly represents an advance and is suitable for publication in AMT.

The authors should respond to the detailed comments below. The most important general comment is that the methodology for calibrations against reactive nitrogen species and the associated uncertainties should be made clear. For example, I did not find descriptions of how the independent measurements of NO₂, PN or AN test compounds were made (perhaps I missed it – in any case, it should be better highlighted). The statements about HNO₃ lack any description of inlet effects, which are known to be severe for this compound. Notably, the paper does not present in-flight data for this compound that would demonstrate the time response of the inlet. Some comment on this aspect is warranted.

Response:

In paragraph 2.4 is reported the calibration procedure that, as reported in the manuscript (page 8769, lines 12-16), involves only NO₂ because all the cells measure NO₂; by thermal dissociation Σ PNs, Σ ANs and HNO₃ achieve complete dissociation into NO₂, therefore there is a 1:1 correspondence between the NO₂ produced by thermal dissociation and the concentrations of Σ PNs, Σ ANs and HNO₃ (Day et al., 2002). Regarding the effect of the inlet on the HNO₃ loss, as described, we used a PFA tube for the common inlet and, as reported in the Fig. 1, we

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heated it to reduce the HNO₃ absorption. We will describe it clearly in the revised manuscript (page 8766, line 6) to read as follows: "The first part of the common inlet is heated (Fig. 1) to minimize HNO₃ wall loss (Neuman et al., 1999; Day et al., 2002)." The aim of this paper was to describe the instrument, its laboratory tests and show some examples of in-flight data to be compared with other instruments. Forthcoming papers will be devoted to describe and analyze in details in-flight data.

Specific comments:

Page 8762, line 11: PN's do not require a temperature change to transport NO_x. They will release NO_x in a more dilute air mass due to their equilibrium with NO₂.

Response:

We agree with the reviewer, so we have rephrased this sentence to read as follows: "Consequently, because Σ PNs are stable at low temperature and they have a lifetime of several months in the colder regions of the atmosphere (mid to upper troposphere or high latitudes), they are reservoirs of NO_x and they can undertake long-range transport."

Page 8762, line 17: N₂O₅ should be multiplied by two in total reactive nitrogen.

Response:

This is correct: done.

Page 8765, lines 15-17: Please define what a "supercharger" is (not a familiar term to this reader). Also, define the abbreviation "PMT"

Response:

The supercharger is a modified automobile supercharger used as a small roots blower because it is lighter than conventional roots, we will clarify this in page 8765, line 15 to read as: "The air flow is ensured by a modified automobile supercharger (Lysholm 3300), used as a roots blower". PMT is a photomultiplier, it will be specified in the

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revised version the first time it is mentioned (page 8765, line 17).

Page 8765, line 23: Although it's a minor point, some statement of the NO₂ fluorescence excitation spectrum is helpful here. For example, over what range of wavelengths does it fluoresce when excited at 532 nm? What fraction (approx.) is collected by this arrangement, and where does the PMT sensitivity fall off? Why use long path filters that are 100 nm removed from the excitation wavelength?

Response:

We have not reported all these details here, because the detection system of the fluorescence is one of the parts of the instrument already described in one of our previous works (Dari-Salisburgo et al., 2009). Even if in the paper we suggest to refer to that paper for more details on this part, here we can give again some information: 1) When NO₂ molecules are excited they show a red-shifted fluorescence, therefore they fluoresce at wavelength longer than 532nm. The aim of using a long-pass filter with a band-pass 100 nm red-shifted from the excitation wavelength is to remove the very strong Rayleigh scattering, that is more intense than the fluorescence and happens exactly at 532nm, and to remove also the Raman scatterings that is around 610 nm. The PMT cut-off wavelength is 950 nm and its quantum efficiency is 10% (Dari-Salisburgo et al., 2009).

Page 8766, line 25-28: The temperature set points are evident, as stated. Are the retrieved mixing ratios for each nitrogen species also quantitative?

Response:

As reported several times in paragraph 3 during the laboratory tests we detected concentrations of nitrogen species very close to what generated and sent to the inlet.

Page 8767, line 14-16: Does the residence time in the upper part of the inlet need to be as large as 0.4 s? This could be an opportunity for improvements in future designs to achieve faster time sampling response (e.g., 0.1s, which is the stated data

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reporting rate).

Response:

The residence time achieved is enough to exclude secondary chemistry, and it is similar to that of Day et al., 2002 instrument for the inlet, heater and considering all the line. However a faster time sampling would be a further improvement of the system as correctly suggested by the reviewer.

Page 8768, bottom: For the HNO₃ channel, does the accuracy include losses in the unheated section of the rear-facing inlet outside of the aircraft?

Response:

Yes, the accuracy reported includes the rear-facing inlet and was evaluated in the aircraft set-up.

Page 8769, line14-16: Two comments, related to those above. First, a quantitative calibration for AN, PN and HNO₃ should be shown, or at least referenced from other work, rather than the statement that the observation of temperature thresholds is sufficient to infer quantitative conversion. Second, while it is plausible that AN and PN will go through the inlet quantitatively, it is much less likely that HNO₃ will do so. Is there an associated uncertainty for loss of HNO₃ (or loss of time response) on the inlet?

Response:

The system is calibrated for NO₂ because all the cells measure NO₂ (ambient or that produced by thermal dissociation of nitrates and HNO₃). As reported in the paper (page 8769, line 16), previous works have showed that each molecule of nitrates or HNO₃ produces one molecule of NO₂ at the right dissociation temperature. A detailed proof of this 1:1 correspondence can be found in the following papers that we add to the reference list: Hao et al., 1994; Zabel, 1995; Kirchner et al., 1999. Regarding the HNO₃ loss we used a PFA tube and we heat it to minimize the wall loss, we made tests to see if the absorption on the tube walls is important and we found that it is minimal and well

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within the errors of the measurements.

Page 8769, bottom, and Figure 5: Figure would be more helpful if the x-axis were in seconds (or minutes) to assess the time response shown. Also, should one expect the NO₂ response to be constant, or was the variability in the delivered NO₂ source? The mixture was “about” 0.8 ppbv NO₂, 3 ppbv PAN, and 4 ppbv ethyl nitrates. How are these determined independently from the TD-LIF? Finally, the legend in the figure does not match the numbers in the text (i.e., NO₂ in the figure is 4 ppbv, not 0.8).

Response:

In the revised version we have changed the x-axis labels that now are in hh:mm:ss. Yes, it is correct: the variability of NO₂ is due to changes in the delivered NO₂ source. The NO₂ concentration is determined independently from the TD-LIF using the calibration system, whereas PAN and ethyl nitrates are estimated from their dilution and flow. The legend of figure 4 was a typo, it is corrected now, to read as follow (page 8769, line 20): “A mixture of about 4 ppbv of NO₂, 800 pptv of PAN and 3 ppbv of ethyl nitrates. . .”

Page 8771, line 20: This is a convincing demonstration of the separation between the PN and AN channels. Is there a similar specificity in distinguishing HNO₃ from ANs? (in other words, the AN heater does not convert HNO₃)

Response:

Yes, we are sure that the ANs heater does not convert HNO₃ and this is evident in figure 3. Other tests, not reported here, show that below 550° C the conversion system does not dissociate HNO₃, and since the temperature used to convert ANs is below 450 ° C we are more than sure that it is not converting HNO₃.

Page 8773, lines 18-20. Give the stated accuracies of the two NO₂ instruments here to assess whether the agreement to within 9% is consistent with those stated accuracies. A 9% disagreement for an NO₂ comparison is probably not “excellent,”

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though I would leave this only as a suggestion to the authors to choose a different description. Any additional speculation here on the possible reasons for this difference would be helpful to the reader.

Response:

We defined "excellent" the agreement between the NO₂ measured by the TD-LIF and that measured by the chemilum., because it is an intercomparison in the atmosphere and on-board an aircraft with inlets 8 m apart and because it is a result comparable or even better than NO₂ instruments intercomparison performed inside a reaction chamber (Fuchs et al, 2010).

Page 8774, line 14: A few questions here. First, should the PN channel detect N₂O₅ as 1xNO₂, or 2xNO₂? Provide some statement of the expected conversion of the nitrogen in N₂O₅ in the PN channel. The slope in the scatter plot is given as 0.78, with the N₂O₅ lower than the PN. Is this due to larger than unity conversion on the PN channel (i.e., actual expected slope should be 0.5), or because the signal on the PN channel is due to more than just conversion of N₂O₅? Or is the difference attributable to instrumental error? What temperature is expected to result in quantitative dissociation of N₂O₅ in the PN inlet? Have the authors considered the effect of other reactive nitrogen compounds, such as ClNO₂, which is likely to be present together with N₂O₅? What is the likely effect of this compound on the measurements in figure 10? Reference to the work of Osthoff's group would be useful here.

Response:

The Σ PN channel detects N₂O₅ as 1x NO₂ because, when heated, each molecule of N₂O₅ produces one molecule of NO₃ and one of NO₂. From laboratory tests, where a known amount of N₂O₅ is sent to the TD-LIF and the BBCEAS, the conversion of N₂O₅ in NO₂ is completed at about 90° C, after this temperature there is a plateau, where concentrations do not change up to 200° C (paper in preparation). The 0.78 slope, as reported in the paper, is due to other PNs nitrates detected by the TD-LIF but not observed by the BBCEAS. We exclude the effect of ClNO₂, because,

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we expect to detect this compound in the Σ AN channel (Osthoff et al., 2008, Thaler et al., 2011). In the Σ PN channel we expect other PAN compounds, therefore we add the following sentence (page 8774, line 15) to read as: "The slope below the unity is due to other PNs species detected by the TD-LIF but not measured by the BBCEAS, like PAN, PPN or MPAN, which may be significant fractions of Σ PNs (Wooldridge et al., 2010)."

Figure 1: A minor point, but the schematic as shown indicates the Nd:YAG laser to be outside of the aircraft. There is plenty of white space in the diagram to fix this.

Response:

In the revised version we redrew the instrument schematic to house the laser "inside" the aircraft.

Figure 6: Font on axes too small to be legible

Response:

The font of this figure has been increased in the revised version.

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

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