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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.

Anonymous Referee #3

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General comments:

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

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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.

Specific comments:

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

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

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

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?

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

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 reporting rate).

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?

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?

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).

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)

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," though I would

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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.

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.

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.

Figure 6: Font on axes too small to be legible

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