**Atmospheric
Measurement
Techniques**
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Discussions

Interactive comment on "Efficient photochemical generation of peroxycarboxylic nitric anhydrides with ultraviolet light emitting diodes" *by* N. D. Rider et al.

Anonymous Referee #2

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This work presents an updated method for the production of acetyl peroxynitrate species including PAN, PPN, PiBN, and PnBN. The novelty of this work lies in the authors use of UV-LEDs as the light source in place of the standard Hg lamps used in the photo-production via ketones. As a member of the field I fully appreciate the advantages of UV-LED over HG lamps in terms of lower power consumption and heat loadings. However, the paper fails to fully convince the reader with significant hard evidence of the other benefits of this method the authors claim. Particularly, the section in which GC chromatograms are compared to show (1) UV-LEDs are more efficient at forming APNs and (2) less side products are formed using UV-LED methods. In

both cases only a single comparison is given with no statistical analysis showing that the small differences observed are significant and repeatable. As this is the heart of the paper, more focus in terms of actual laboratory evidence should be placed on the comparison of the two methods. The paper in general is well written, and presents a very through discussion of the theoretical yields from these reactions, a very nice supplementary discussion to the laboratory work. I would recommend this for publication following minor additions and changes to the manuscript as described below.

Specific Comments:

P907, line 10: This sentence is not entirely true as some of the chemicals that you are using would be considered hazardous waste. Relative to synthesizing PAN using wet chemical techniques the synthesis methods described in this work are safer, but not entirely without hazard.

P907, line 26: Why make such a statement here, this sounds like a critique of this previous work. Unless there is a reason for mentioning this lack of GC work you should remove this statement, or choose to elaborate as to why this matters.

P909, line 18: There is no Figure S1 in the supplement, Figure A1?

P910: There are a lot of details on the manufacturer of components and it makes this section extremely choppy and difficult to read. Many of these details are unnecessary (e.g. MFC types, data acquisition boards) as any given company or model could be used in place. I suggest only putting in details for products that are essential to this particular set up, such as the LEDs.

P911, line 15: Peroxycarboxylic nitric anhydrides? Of do you actually mean "nitric anhydrates nitrates"

P911, line 21: Perhaps add the Wild et al. 2014 ES&T citation that is about this exact type of cavity ringdown instrument using O3 addition.

P911, line 23: e.g. means "for example" thus you should delete "because of"

P912, line 1: What is this effect due to? Direct interference by DIPK or DNPK? I realize you attempt to answer this in the discussions section but I think this belongs here instead.

P913, line 17-22: Is this discussion necessary? If you are going to describe this then you should comment on the impurities.

P914, line 6: How do you know the remainder is NO2?

P915, line 23-26: The difference for PPN in 4a is very small. Is this difference significant or is this an ideal result that shows the difference? How reproducible is this? This is a weak point in the work. Convince the reader this difference is reproducible and significant.

P916, line 5: "varied to vary", this is awkward

P917, line 18: Respectively to what?

P917, line 24: Figure 4 fails to convince me of this. The differences in peak areas are so small that without a proper error analysis I am not convinced that this difference is statistically significant. Also, I do not see the additional impurities that the authors are referring to. These are some significant point the authors use to suggest that the LED system is advantageous, and therefore need to be shown in a more convincing manner.

P919, line 22: Once again I do not think that you have thoroughly illustrated this.

P920, line 6-7: What is negligibly small in this case. If you are presenting these sources as a method of calibration that can be analyzed using the theoretical calculation of concentrations rather than an actual secondary calibration for validation, than you need to show the absolute potential error in this synthesis method.

Section 4.1: This should be moved to the very end of this manuscript. Ultimately showing that this method of synthesis, using the LEDs, is the novel part of this manuscript.

You need to do a better job of convincing the reader that, other than the improvement in power consumption, this is an improvement on other techniques.

Section 4.2 and 4.3: This is information that can be useful presented earlier in the manuscript, such as when you are initially speaking of the interferences and secondary products in the sources. Overall I think this work could use quite a bit of reorganization to improve the flow and readability of the manuscript.

Figure 1: While this picture is nice, it does not illustrate how the LEDs are oriented on the photolysis cell, which is the heart of this manuscript. This should be made clearer here or in an inset diagram.

Figure 2: This figure cold be improved if you include the precursor compound in the legend or description.

Figure 3: Why are the GC units not in concentrations, but in Figure 2 they are in concentrations? The calculated NO trace should be indicated that it is presented on the left axis. The black NO trace is nearly identical to the zero line. Please modify the zero line to be dashed or color the NO to better separate them.

Figure 4: Perhaps shade either the red or blue curves to better illustrate the area since the lines overlap. I would prefer to see an average chromatogram with standard deviations presented here to inform the reader weather or not these differences are significant.

Figure 5: It was not clear in the text why two different GC systems were used. It is mentioned in a single sentence that the Varian was used for some samples. Why? This needs to be made clearer in the text. Otherwise I am asking myself why you didn't run the PPN on the varian or the PnBN on the HP.

Figure 6: Please increase the font size on the legends. Also please retain the order of the legends, e.g. list the PAN species first or NO first in all panels.

Figure A1: Please increase the font size on all of the labels, or this will be extremely

difficult to read. Also is this a commercial design or is it something that you have made in your lab? Please indicate this better.

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