Review of “Airborne measurement of peroxy radicals using chemical amplification coupled with cavity ring down spectroscopy: the PeREAS instrument” by George et al.

This paper describes characterization of and sample data from an instrument based on chemical amplification and cavity ring down spectroscopy to measure the sum of peroxy radicals (HO_2+RO_2). Described are several instrument tests, laboratory evaluations and box modeling of the instrument performance and optimization. These include assessing the effects of environmental conditions and instrument parameters on its behavior.

This is a useful report of the status of this instrument and should be published. This reviewer has several comments and questions related to topics ranging from general philosophical issues to minor typographical errors.

General comments and suggestions.

The researchers appear to accept the basic characteristics of the inlet/reactor as given. The paper does not justify the selection of flow rates, inlet/reactor volume and composition, and thus the corresponding reaction time. This reviewer sees this approach as flawed. Perhaps this has been well thought out, and previously published, but not included in this paper. Suggest that the authors include some discussion of why these parameters were selected, and what the compromises and advantages in their selection are. One aspect is that higher NO levels used in the studies reported in this paper (30-45 ppmv) result in lower sensitivity to CH_3O_2 (and other RO_2) compared to previous values because of a faster rate of CH_3O+NO+M. High NO also converts a greater fraction of ambient ozone to NO_2, although complete conversion is not necessary. Most other chemical amplifiers used NO reagent mixing ratios of 2 to 6 ppmv.

It is not apparent why the response time of the system is so slow. For example, the Figure 5 caption states that 20 seconds is eliminated after change in NO_2. Given a reactor transit time of 3 seconds, this seems extreme. There may be delays, which can be accounted for in data analysis, that are different than transition to the correct value after perturbations. Part of the answer may be in Figure 19, where step functions in the O_3 concentration result in perturbations lasting about 40 seconds. Also, in Figure 20, the pressure variations last for a long time during and after altitude changes. There are also pressure fluctuations even when the aircraft is not changing altitude. This implies need for better pressure control. Perhaps the PID parameters of the pressure controller have not been adjusted properly. This is very important to get correct. Though improved, such fluctuations are still apparent in Figure 23. They add unnecessary noise to the measurements. Suggest adding more discussion of the pressure control system (manufacturer, model, adjustment procedures) and the response time of the system to step changes in NO_2 concentrations to allow the reader to better understand these issues.

Finally, why are the chain lengths reported in this paper so much lower that previous publications (Table 3)? In fact, values reported in this paper (28-38, Figure 18) are much lower than what is reported under “This Work” in Table 3 and would be the lowest values for the CO/NO chemical amplifier in the table (there are lower values for the ethane/NO chemical amplifier). This compromises the potential quality of the measurements. Perhaps this bears on the question about optimization of the instrument earlier. It seems that chain lengths of 100 or more are possible (at lower reagent NO mixing ratios). Some explanation in the paper is needed to explain this.

The English in this paper is really quite good, but there are few suggestions for improvement given in the specific comments below.

Specific comments and suggestions.

Page 1, line 16. "…for the airborne measurements in the…"

Page 1, line 18. "…instrumental channels successfully captures short term…".

Page 1, line 20. Not sure why the word "gradients" is used here. How about "…range of atmospheric pressures and temperatures expected…"?

Page 1, line 24. The phrase "…collectively known at RO_2*…". Is it true that HO_2+RO_2 is "known" as RO_2*? Is this the term accepted by the community? This reviewer suggests just using "HO_2+RO_2" instead.

Page 1, line 29. Suggest removing the summation symbol, since there is a plus sign used.

Page 1, line 32-33. Suggest "…photolyzed to ultimately produce…"

Page 2, line 34. Suggest "Overall, HO_2+RO_2 influences the…"

Page 2, line 41. Not sure what is meant by "those RO_2".

Page 2, line 43. Suggest "…compared to the total amount of HO_2+RO_2, with HO_2…"

Page 2, line 53. Should be "Kanaya".

Page 2, line 54. Suggest a different word than "largely". Suggest "The interference by some RO_2…"

Page 3, line 72. Add space "Peroxy Radical…".

Page 3, line 74. Suggest "…in a previous publication…".

Page 3, line 79. Suggest "…where ΔNO_2 is the NO_2 formed…"

Page 3, line 84. Suggest "…spectroscopic measurement technique…"

Page 3, line 87. NO_2 comes from radical amplification and from the background (O_3 conversion). Suggest changing the sentence to reflect this.

Page 3, line 92-94. Suggest also saying that c_0 is the speed of light in a vacuum (stated later in the paper).

Page 3, line 92. Suggest "…are, respectively, the absorption…"

Page 3, line 95. Suggest "…used for ground-based measurements…"

Page 3, line 96-7. Suggest "…the particular constraints related to airborne measurement…".

Page 3, line 99. Suggest "In this study, the specifications…are described based on thorough laboratory…"

Page 4, line 107. Suggest (if correct) "…and located outside the HALO fuselage…"

Figures 1, 2, and 3. While photographs can be nice, schematic diagrams are more useful to see the path of sample, reagents, and signals throughout the system. Suggest limiting to only one or two photographs and add diagrams to show the details.

Page 4, line 117. Mixing and pressure regulation are mentioned here, but no detail is given. This is relevant to the general comment given earlier. Suggest adding more detail in the text and perhaps in Figures 1 and 2. Suggest discussing how DUALER I and II are different and describe why the changes do indeed result in improved performance.

Page 4, line 124. The term "piezo electric stack" is not a common term and needs more description.

Page 4, line 128. Suggest adding the manufacturer of the beam camera (MKS Ophir). This is very cool, by the way!

Page 4, line 132-3. Suggest "…other sensor data such as pressure, flow, temperature, and humidity." You don't need "etc." if using "like" or "such as".

Page 5, line 149. Would "occasionally" be better than "exceptionally"?

Page 5, line 150-152. The term that should be used is “Allan Variance” rather than “Allan Deviation”. Perhaps the equation for its calculation should be given, since there is also modified Allan Variance that can be used. Also, give one or two references (e.g. Allan, 1966; Allan et al., 1991; Allan and Levine, 2016). Suggest “…was investigated using calculated Allan Variance in the measurement…”. Also “…the optimum integration time for the three PeRCEAS detectors is between 20 s…”. Do you use 20-30 second averaging in the data analysis? The timing of the instrument cycling should be shown, perhaps in Figure 1 or in a separate figure.

Page 5, line 155. The phrase “…over the modulation time…” need explanation. This might be apparent with addition of a figure showing the instrument cycle timing.

Page 5, line 161. Suggest “…signals generated that minutely varied the sampled NO_2…”

Page 5, line 164. “…time resolution using each background…”. This will be more obvious with a graphical representation.

Page 5, line 167. “… molecules cm^{-3} for typical measurement conditions”.

Page 5, line 170. “It is inferred from laboratory calibrations that a 60 s modulation cycle is an optimum comprise between…”. The term “modulation cycle” is not apparent here, but perhaps would be with a graphical representation of the instrument cycle. Also, add more discussion why fluctuations last so long (20 s).

Page 5, line 172. The detection for NO_2 should be performed with a background level of ozone in the sample, since this is how ambient measurements are performed. Was this is the case?

Page 5, line 173-4. It is not obvious that larger modulation times lower the representativeness of the averages. Do you mean variability in peroxy radicals or in the background? For the latter, the instrument is continually measuring the background, and it should be well accounted for. If you mean the peroxy radicals, while one-minute (or quicker) data are nice, longer averages can still be useful in adding understanding of tropospheric free radical behavior. Suggest rewording the last sentence of this paragraph.

Page 6, line 176. “Sample and reagent gas flows...”.

Page 6, line 176-184. This discussion of reaction time should also include discussion of how the size of the reactor was selected, since it also affects the reaction time (reactor volume / total flow). Perhaps this would be a good place to discuss the approach to ensuring mixing of reagent gases with the ambient air sample. How was this done? Were fluid dynamical calculations performed? Were flow visualization approaches used? Related to this: how do you ensure that no components of the inlet system are leaking?

Page 6, line 182. “…lower explosion limit (LEL) in air of 12.5% v/v at room temperature…”.

Page 6, line 189. Remove extra space between “air” and “and”, and between “CO” and “in”.

Page 6, line 190. Suggest “…between safety requirements, limiting…”.

Page 6-7. Effective chain length. This might be good place to discuss experiments to determine the optimum NO concentration for the amplifier chemistry. Also, perhaps near the end of this section, discuss how the effective chain length values are used in the data analysis. In other words, have estimates of the HO_2/RO_2 ratio been made and used to apply the two eCL (for HO_2 and $HO_2+CH_3O_2$) values? If so, how is it done?

Page 6, line 197. “…to the conversion into RO_2.”. Include that the approach is based on O_2 actinometry, as opposed to other approaches reported in the literature (such as N_2O actinometry, calibrated NIST photodiodes).

Page 6, line 205. "…are changed stepwise every ten minutes from 8 pptv…". Also, note that too much reagent added to the calibrator has the potential to affect the inlet chemistry. This can be seen by a change in the background with change in radical concentration, which is not expected if the background is mostly due to ozone.

Page 6, line 206-7. "…is determined from the slope of the measured ΔNO_2 levels versus the calculated radical amounts. Example data is shown in…". Suggest rewording the end of the last sentence on this page, since the concentration of NO ***within the inlet*** is 30 ppmv. Perhaps "…and added reagent NO to achieve 30 ppmv within the inlet."

Page 7, line 208. Suggest "In Figure 7, the PeRCEAS eCL versus the inlet NO concentration…". In Figure 7, why aren't data shown for lower NO concentrations, such as used by your group in the past and by other researchers?

Page 7, line 212. "…concentration, eCL values increase with…".

Page 7, line 16-18. Suggest describing how wall losses were determined. Are they constant or are they affected by the cleanliness of the inlet? Suggest putting all the rate coefficients used for both reactor pressures into Table 1. It is interesting that a level of 3 ppbv O_3 was used, presumably because this is what comes out of the calibrator. Suggest also running the model with ambient-like levels of O_3.

Page 7, line 221. Inlet pre-chamber is not defined anywhere. This should be shown in the schematic diagram discussed earlier. If the radical losses in the model do not agree with what you think they are in the DUALER II inlet, suggest you perform experiments to determine what they are. The model of this simple chemistry should be much closer to the observations that a factor of two!

Page 7, line 222. Suggest "…shows measured eCL versus modeled CL for the…".

Page 7, line 223-4. "The $CL_{modeled}/eCL_{measured}$ ratio averages about 2 for HO_2…". Actually, the ratio is more than 2 for the 200 mB measurements and is about 2 for the 300 mB HO_2 measurements. Only the 300 mB HO_2+CH_3O_2 measurements are about 1.5. Does this mean that the inlet wall loss changes with reactor pressure? Were the rate coefficients in the model changed to reflect the reactor pressure? Perhaps the model wall loss values should be adjusted based on new laboratory measurements. The chemical amplifier chemistry is simple enough that a box model should be able to accurately reproduce laboratory data such as this. Add error bars to the points to represent total uncertainty in the measured and modeled values. Perhaps perform regressions of data.

Page 7, line 226. This reviewer does not like the term "titration" in this context, even though it is widely used in the community. Suggest using "conversion" instead.

Page 7, line 227. This reviewer disagrees that ozone in the sample has to be completely converted to NO_2. Why is this? It seems that partial conversion, as long as it is stable, would be fine.

Page 7, line 228. Figure 9 has a lot of information that could be presented in a more straightforward way. Suggest plotting the ozone lifetime (or three lifetimes) versus the reactor NO at the two pressures. This could be shown in one plot.

Page 7, line 229. There is no reason to require conversion of 100-200 ppbv of ozone to 1-2 pptv in the inlet. Conversions of 99% are more than sufficient. Suggest changing this paragraph as Figure 9 is changed.

Page 7, line 230. The wavelength 409 nm is mentioned, but everywhere else it indicates that the lasers operate at 408 nm.

Page 7, line 236. Suggest "…which are captured by…". This reviewer disagrees that the radicals and NO_2 from PAN-like compounds cancels and does not lead to interference. Yes, the NO_2 from the decomposition should be like ambient NO_2 and be corrected for by the background measurement.

But the radicals formed from the decomposition will amplify and appear like ambient radicals. This is an interference! Suggest rewording this paragraph. Some direct laboratory measurements of the interference would also be helpful. Figure 11 shows that the PAN interference is greater at lower reactor pressures. Why would this be the case. At reduced pressure, the decomposition is slower and the time is the reactor is shorter. Suggest checking the modeling.

Page 8, line 259-260. It is not clear what is meant by "based on the similarity of the eCL values". Suggest rewording this sentence, and perhaps this entire paragraph to make the message clearer.

Page 8, line 263. Suggest replacing "as shown exemplary" with "with an example shown".

Page 8, line 265. "…sample humidity do not lead to…".

Page 8, line 267. "…is subject to two types of errors which either are: a) intrinsically…"

Page 8, line 268. "…in the laboratory, or b) result…"

Page 8, line 273. Equation 3 is very similar to Equation 1. Suggest eliminating Equation 3 and referring back to Equation 1 in this discussion. Perhaps change Equation 1 slightly, if needed.

Page 9, line 279. "…Vandaele et al. [2002] with the normalized laser spectrum from the corresponding detector.". Also, "The values obtained have been…"

Page 9, line 284. "…depicts a sample comparison of spectra…".

Page 9, line 294. "The effective σ_{NO2} obtained agrees within…".

Page 9, line 297. The tau symbol disappeared. You have a lot of ambient data. Does τ_0 vary significantly as the CRDS cell mirrors are exposed to ambient air?

Page 9, line 300. "…measurement requires accurate…"

Page 9, line 302-3. "…are the radical calibration…". "…which is estimated to be…".

Page 10, line 307. "The errors associated…".

Page 10, line 312. "…reactor 2, respectively, and…".

Page 10, line 315-6. Delete "during the airborne measurement of RO_2*".

Page 10, line 317. "The noise in the NO_2 signal is enhanced by…".

Page 10, line 319. "…cabin temperature could increase…".

Page 10, line 320. "…stability of the CRDS signal and the accuracy of the supporting measurements.".

Page 10, line 323-4. Again, this reviewer does not agree with this statement. Since you are continually measuring the background and the amplified signal plus background, variations should be accounted for. Only changes happening faster than one second should have influence, unless there is something about the data analysis that is not obvious from the presentation in the paper. Suggest looking into why step changes in ozone should affect the signal for more than a few seconds. Also, step changes are extreme for ambient measurements. Even changes as the aircraft changes altitude are likely to be gradual unless a pollution layer is encountered.

Page 10, line 335. "…a standard deviation of the order of…".

Page 11, line 353. "…detector signals can be significantly affected…".

Page 11, line 360. "…airborne measurements and is difficult to implement in…".

Page 11, lines 364-370. Do you mean running the inlet at reduced pressure results in lower eCL values? Doesn't PeRCEAS continually measure the signal and background as mentioned in the second line? What do differences in detector accuracy (do you mean sensitivity) do to affect their uncertainties? Suggest adding a reference to the last sentence of this paragraph (about RO_2 interferences in LIF).

Page 12, line 374. "Figure 20 shows sample data of RO_2* measured…".

Page 12, line 382. Mention that the flagged values are shown in Figures 20 and 23. Also mention this in the figure captions.

Page 12, line 386. "…in more detail in Figure 23…".

Page 12, line 388. Not sure what is meant by "the signal is not affected by altitude changes", since there are jumps in ΔNO_2 when the altitude changes. Suggest rewording to make the point clearer.

Page 12, line 402. "…over a 60 s integration…".

Page 12, line 404. While PeRCEAS may be suitable for measurements up to 12 km, no data were shown at this altitude. Suggest rewording this sentence.

Page 12, line 405. "…campaigns onboard HALO.".

References

Line 449. "…peroxy radicals by chemical amplification…".

Line 452. Two references are together. Need carriage return after "1993".

Tables

Suggest heading for "second addition point" to be changed to "reaction times", and "to detector" changed to "transfer times".

Page 3, Edwards et al., Inlet pressure should be 200 mB.

Figures

Most of the figures need larger symbols and bolder lines (4, 5, 6, 10, 12, 14, 17, 18, 19, 20, 23). In many of the plots, the legend is covered by data. Suggest enclosing legend in a box with a white background.

See comments earlier about Figures 1-3.

Figure 2 caption. "…Top view of the…". "..the laser beam is highlighted (purple) for…". "…exiting the cavity is depicted."

Figure 4. Change y-axis to Allan Variance. Describe what the lines depict (linear fits to data less that 10 seconds?). Can you sample for longer times than 70 seconds? Suggest doing the analysis out to 10 minute averages or more.

Figure 5. It is not obvious what this figure is trying to show. It appears to this reviewer that the point is temperature changes affect the τ_0 of the detector, but the retrieved ΔNO_2 is affected very little. Why not do this experiment with two detectors as done for radical measurements? This would be a more realistic representation of the actual measurement situation.

Figure 6. Are the equations determined from linear fits? Are they standard or bivariate fits?

Figure 7. Why are not data shown for lower values of NO? Suggest more work going from 0 to 3.5E14 NO with at least 10 points for each instrumental condition (pressure and radical type). Perhaps also show the same y-axis for both plots.

Figure 8. Since it is mentioned in the text, suggest adding 1:1.5 line. As discussed earlier, perhaps more modeling with more realistic wall loss rates needs to be done.

Figure 9. Changes to this figure suggested earlier (plot O_3 lifetime versus NO). If it is kept the same, suggest labeling each sub-figure and referring to those labels in the caption.

Figure 10. This shows that 60% of the O_3 is converted with NO of 3 ppmv, and 90% at 6 ppmv. This means that the instrument could be run with much lower NO levels.

Figure 11. It is stated that PAN interference is not a problem with PeRCEAS, but this plot shows that with reaction times of 3 seconds (compared to 2.6 to 3.1 seconds for the two DUALER inlets), up to 6 pptv of peroxy radicals can be produced from 1 ppbv of PAN. Is this representative of the conditions for which the instrument has been used? This figure could be changed to plot the fraction conversion of PAN (CH_3O_2 produced / PAN) versus temperature for the two DUALER reaction times.

Figure 13. There are places where the ambient water is below the inlet water. How can this be? This figure could be changed to plot inlet H_2O versus ambient H_2O with the points colored by altitude.
Figure 14. How can the lack of dependence on water vapor be explained, given that it is a purported to be related to one of the amplification chemistry reactions (HO_2+NO)? Perhaps modeling of these data would be instructive. Also, suggest showing data down to the lowest water values possible.
Figure 15. Can the laser emission be adjusted so all three detectors peak at the same wavelength? This would definitely help them to behave more similarly. Suggest changing the right-hand y-axis to go from 0 to10, and to average the cross-section data to a lower resolution, say 0.1 nm, to make the plot message clearer.
Figure 16. Not sure this figure is necessary, since the data are plotted in Figure 17.
Figure 19. change caption "..while changing O_3…", "…in the source with estimated 15%...". It is not clear why the perturbations to ΔNO_2 last so long (up to 40 seconds) when the background should be measured on the 1 second time scale. Is this a data processing issue? Suggest checking why this is the case.
Figure 20. There are big swings in the inlet pressure even when the altitude is not being changed. Why is this?
Figures 21 and 22. These figures could be eliminated.