

## ***Interactive comment on “An Automated On-line Instrument to Quantify Aerosol-Bound Reactive Oxygen Species (ROS) for Ambient Measurement and Health Relevant Aerosol Studies” by Francis P. H. Wragg et al.***

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Answers to Review comments for “An Automated On-line Instrument to Quantify Aerosol-Bound Reactive Oxygen Species (ROS) for Ambient Measurement and Health Relevant Aerosol Studies” by Francis P. H. Wragg et al.

Anonymous Referee #2 This manuscript presents an innovative and practically promising analytic technique to detect aerosol-bound ROS in ambient environment. The work integrates the wellknown DCFH ROS detection assay into a portable instrument, which executes a complete analysis including sampling, sample preparation, and detection.

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The technique is promising to be applied in practice to detect aerosol-bound ROS in the real atmosphere and the authors also demonstrated this with an urban roadside site. The result of the filed study is intriguing in the observed correlation between ROS concentration and the PM<sub>2.5</sub> measurement. I take this paper a good match to the theme of AMT journal. Therefore I recommend the publication of this paper. However, there are still some scientific questions that the author should consider revising.

1) In this work, H<sub>2</sub>O<sub>2</sub>/HPR assay was used to calibrate the instrument, and the active ROS here is H<sub>2</sub>O<sub>2</sub>. The same HPR assay is also used for aerosol particle bounded ROS detection. Does this mean only H<sub>2</sub>O<sub>2</sub> species can be detected? The authors are encouraged to elucidate what ROS species can be detected by this technique.

See also the response to question 8, reviewer 1. As described in section 3.1 (lines 265-270), the HRP/DCFH assay is sensitive not only to H<sub>2</sub>O<sub>2</sub> but to a range of other oxidizing compounds. We evaluated the response to organic peroxides and organic peroxy acids both of which react with HRP/DCFH. It is possible that other compound classes also react with HRP such as peroxy radicals PAN-type compounds but this was not tested in this study.

2) The authors suggest 12 minutes a “suitable value” as a time resolution. A more thorough discussion of this conclusion is expected. It is hard to read the 12 minutes from Figure 6. From my understanding, 12 min is claimed to be the time interval of the reaction to reach a steady state, the instrument at which is used to calculate the ROS concentration. This time length should also be validated for the case of H<sub>2</sub>O<sub>2</sub>, which is used a standard solution for calibration.

See also the response to question 7, reviewer 1. It is now more clearly described in line 342-347 how the time resolution was derived. The times resolution is similar (slightly improved) for H<sub>2</sub>O<sub>2</sub> calibration solutions.

3) The authors found different ROS/aerosol ratio with different UV lamp power. Although a “probable” explanation is provided, the authors are encouraged to add more

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work to test their hypothesis if possible. Other than the consideration of compounds' volatility suggested by the authors, other reasons remain, e.g., the different reactivity with HPR in the two cases.

Based on the above comments, it seems this figure has brought unnecessary confusion onto this manuscript, detracting from its main purpose of describing the instrument and its performance. We have thus replaced details of that specific experiment in section 3.2 (and therefore also the related figures – figure 5, figure 6, and figure 7) with those of an experiment using one lamp only (see lines 287-289 and 303-304). Specific description of the previous setup using two UV lamps has now been removed. This section now conveys a simplified message; that increased mass of oxidised SOA leads is linearly correlated to ROS and OP-ROS detector signals.

Besides the issues above, some sentences in the manuscript should be more quantitative. A few specific comments are as follows:

4) L40-45; L115: The authors mentioned the disadvantage of traditional techniques at multiple positions through the paper, without explicitly introducing what are these techniques. A clear identification of them helps readers to understand why they have these disadvantages.

We now reference a few studies which use traditional offline techniques, during our discussion of offline disadvantages, in lines 122-125.

5) L161: what are the suitable time and temperature?

The paragraph at the beginning of section 2 (line 153-160) gives a general overview of the instrument. Detailed operating conditions, including temperatures and reaction times are detailed in the rest of section 2. See line 167 for specific details regarding time and temperature.

6) L281: how quick is "quick-reacting"?

It is now more clearly described that the instrument is most sensitive to ROS that react

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within 10-15 with HRP/DCFH (line 272-289).

7) L380-385: It is a good strategy to compare results of real atmosphere measurement by this work with existing studies. However, there are more studies existing with similar data reported. Some of them are cited in Wang's work (Wang et al., 2011). The authors can compare their results with more work.

Some of these other studies are now mentioned (see line 365-372).

8) L420 Figure 4: What's the meaning to use a nonlinear regression for the calibration curve?

A nonlinear shape was only observed at high concentrations above 2  $\mu\text{M}$   $\text{H}_2\text{O}_2$ ; likely due to eventually surpassing a maximum production rate of fluorescent product per  $\mu\text{mol}$  reactant added. Such high signal intensities are only seen at very high SOA concentrations, likely only possible to be generated within a flow tube setup, and are not expected to be encountered in the ambient atmosphere, or in atmospherically relevant laboratory/chamber studies. Thus, this figure has been updated, and now shows the calibration curve only up to 1  $\mu\text{M}$   $\text{H}_2\text{O}_2$ , a suitable range for ambient and lab/chamber studies, showing a linear relationship within this concentration range.

9) Technical corrections: L268: the unit after 0.25-0.5 is blurred. It should be  $\mu\text{M}$  according to Figure 4.

Corrected. See line 260.

The following additional changes were made to the manuscript:

10) Slight alteration to fig 1: switched the positions of the silica drier and mass flow controller. Their relative order was incorrect in the previous version of the Figure.

11) Various changes to grammar and sentence structure at various places in the manuscript to improve clarity for the reader.

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