

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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Received and published: 14 September 2016

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 #1 This paper presents a new portable instrument to measure particle-bound ROS with the DCFH assay suitable for field deployment. The general method has been previously published, here the unique feature is the portable design. I would not characterize this as a significant advancement in instrumentation, but I can

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image that the design may be of general interest making the paper worthy of publication. The paper is very well written and organized, I have only a few minor comments.

1) Abstract line 63, not sure a 12hr limit allows for extended field operation. I would say it is more like extended field operation if an operator is on site every day.

It is correct that currently an operator needs to check the performance of the instrument twice daily. The operator basically needs to renew the reagents/empty waste but the instrument can continue to acquire data during this. Our instrument is a considerable improvement to any existing instrument and the automated operating design presented here can be increased with minimal changes for future studies.

2) Relating to this: How often does the filter need to be changed, are there issues with accumulation of non soluble species on the filter?

The instrument was tested so far with SOA generated in a flow tube, with SOA generated in the Cambridge Atmospheric Simulation Chamber, and at a roadside location in London, UK. During each of these tests, the filter was changed daily as routine. Requirement to exchange filters is likely to depend on the level of particles in the atmosphere and their chemical composition; this will continue to be assessed to consider if the daily replacement is insufficient for a specific case.

3) How often do the chemicals need refreshing, ie, are the chemicals stable, are there issues with DCFH being stored beside the instrument for long periods, what is the effect of temperature where the system is operated on how long the chemicals are stable? . For example, what is the actual limitation on the extent of time the instrument can be run without attention? In the conclusion it appears to be only the size of the waste and chemical containers that determine the limit, implying really there is no limit if one gets bigger containers.

With the current configuration, full bottles can last 16 hrs measurement. Over this 16hr period, the instrument can be left running unattended. This has now been updated

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and clarified (line 315-317). As stated by the reviewer, this time period could be easily increased by increasing the volume of the reservoirs for the liquid reagents. Chemicals are stable over 1-2 days, depending on temperature and exposure to light. So far the instrument was only operated in air conditioned areas.

4) When adding variable amounts of liquid to the system, and given that some liquid added leaves the system as vapor, which also varies, discuss how overall liquid dilution is determined and factored into the ROS concentration calculation.

The liquid flow leaving the particle collector is constant at 1 ml/min, varying only due to the pump variability (quoted as +/- 1%). This flow joins with flow from pump 3 (also 1 ml/min) in a y-junction, resulting in a 1:1 dilution. The rate of HRP reagent addition to the particle collector, controlled by optical sensors as discussed now explicitly when describing Fig. 3 (line 205-221), maintains the same liquid volume in the syringe (and thus the same dilution of sample-into-liquid). The overall flow into the particle collector over many hours is approximately identical to the overall flow out as only a negligible amount is lost as vapour.

5) Line 78-79, need references.

References have been added. See line 77.

6) Line 215, typo. Also, please add how LOD was determined.

There is now a description of how the LOD was determined (line 334-336).

7) Because this is a bulk reaction system, ie the sample is mixed within a fairly larger volume of water, time smearing of a sample is expected. Does the 12 min time resolution roughly correspond to some measure of response time expected for the volume of liquid in the collection system, say assuming it is perfectly mixed?

12mins is the maximum recorded time of the detector signal to transfer between two distinct sample concentrations upon an instantaneous change. This is now more clearly described in line 342-347.

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8) Lines 272 – 275 are not clear, ie are the numbers, 1.6 and 16.8, how much weaker the response is? If so, what does this imply for the method as a measure of aerosol ROS if the response is specific peroxide dependent? How does one know that in the ambient atmosphere the system is just mainly a H₂O₂ detector? (For more on this see last comment).

Peracetic acid and tert-butylhydroperoxide react by a factor of 1.6 and 16.8 less efficient than H₂O₂ after a reaction time of 10-15 min (these values have now updated to 1.5 +/- 0.03 and 19.3 +/- 2.05 upon improved analysis, respectively). This has now been clarified in the text (lines 265-270), and Fig 4 has now been updated to show this relationship in a clearer way, via comparison between H₂O₂ calibration and the peracetic acid equivalent. With these measurements we show that HRP/DCFH is reacting with organic peroxides and peroxy acids, although with largely varying kinetics, and we determined that peracetic acid is almost as reactive as H₂O₂. Thus, the instrument is not only sensitive to H₂O₂. But we also clearly state in the paper that the overall ROS signal obtained by our instrument is that of fast-reacting ROS (including H₂O₂ and organic peroxides, peroxyacids and possibly other compounds). “Fast-reacting” refers to a time constant of 10-15min, which is given by the reaction time in our continuous flow system (see lines 272-279). We like to emphasise that to the best of our knowledge we are the first who provide reactivity data of atmospherically relevant compounds with the HRP/DCFH system but it is clear that future studies should aim to continue thorough characterisations of ROS quantification systems (not only the HRP/DCFH assay).

9) Fig 8. What are the error bars? How does one know if the variability observed in ROS is not just noise, rather than the instrument responding to something real in the aerosol? Eg, is the ROS correlated with mass ($r=?$ could be added to the figure). Any other data collected at the site that could show the data variability makes sense? Can one estimate the H₂O₂ concentrations at the site and compare the magnitude to recorded ROS (how do you know you are just not measuring mainly H₂O₂)? A much longer time series of data would greatly strengthen this paper. Diurnal profiles could be

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informative (ie, correlation with oxides). This is a major weakness of the paper since the authors are asserting the instrument is designed to run for extended periods with limited attention and a larger data set would prove highly useful in assessing the data generated; the small data set tends to undermine the premise of the paper.

Error bars in Fig. 8 have been updated to represent $1 \times \text{LOD}$ as now explained in the caption for Fig. 8. Fig. 8 is presented to show that the instrument is sensitive enough to quantify ROS at levels encountered in London, UK, not to discuss the implication of the results in any great detail. In a forthcoming publication a more detailed comparison and analyses of these and additional field data will be presented.

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.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-183, 2016.

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