

Interactive comment on “Development, characterization and first deployment of an improved online reactive oxygen species analyzer” by Jun Zhou et al.

Anonymous Referee #2

Received and published: 1 August 2017

This manuscript described the design and characterisation of an online ROS analysis systems very similar to instruments built by other groups before. A number of aspects are not described in sufficient detail and the following points need to be considered before publication.

p.1, line 14/15 (Abstract): it is unclear what the detection limit for offline is. 1.3 or 9-13nmol L⁻¹. Also, indicate with what compound this detection limit was determined. nmol H₂O₂ L⁻¹?

p.2, line 15: Please also reference Wang et al., Journal of Toxicology, 2011, who first developed an online DCFH system.

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p.3, line 12: What is the difference between reaction and incubation?

p.3, line 15/16: For how long was the denuder efficient and how was this assessed? The HRP assay is sensitive to H₂O₂. Was the denuder efficient in removing gaseous H₂O₂? How was that determined?

p.4, line 12/13. Please support the statement in this sentence with evidence. By how much was the lifespan of the solution shortened and how did the additional contamination affect the measurement?

p. 7, section 2.2 I am not sure this section is necessary as it does not add any information.

p.8, line 1: With what experiment was the residence and response time determined.

Fig. 2: How is the difference in detector response reconciled between the two compounds?

p.8, line 8: Was the LOD online determined by using ambient air?

p.9 & Fig.S3: Looking at the data in Fig.S3 and confidence intervals shown it look to me the detection limit is more in the range of 15nM. How does that compare with numbers discussed on p.8.

p.9, line 20: Did the use of ethyl acetate affect the reactivity of HRP and/or DCFH? How was this verified? The enzyme HRP could be strongly impaired in its reactivity in an organic solvent.

p. 10, line 5: Data are only shown from 30-150nM, not 0 – 150nM.

p. 11, Fig. 4: No detail is given for the data shown in Fig. 4. What are the dates, collected? Do they correspond to data shown in the references cited? Why is there a difference in the two data sets, what are the errors on the data shown etc.

p.13, line 14: SO₄ and NO₃ (given in units of ug m⁻³) were mixed with H₂O₂ (given in

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units of nM) for cross sensitivity test. How was that done. Was the sulfate and nitrate nebulised as aerosol? A lot more detail needs to be added here.

p. 14/ Fig. 6: The experiments with $\text{Fe}^{2+}/\text{Fe}^{3+}$ are discussed in a purely descriptive way. A more detailed discussion rationalising the results and referencing Fenton reactions is needed.

p.14, line 11: It is mentioned that water-soluble Fe^{2+} is measured up to 100s ng m⁻³ in ambient samples. To what concentration does that correspond in the working solution. Could the ROS signal potentially be suppressed under these conditions? This should be discussed more clearly.

p. 17/ Fig. 8: Are the units for the x and y axis “nmol H₂O₂ m⁻³”? If yes, this should be indicated explicitly.

p.16, line 15/ Fig.8: It is mentioned that filters were collected before and after the VACES. Was ROS different in the filters collected before and after the VACES? Did the use of a VACES affect online ROS concentrations?

Fig 9 and related discussion: It is not acceptable to derive a half-life of ROS from the data shown in Fig. 9. The time resolution of the data presented is far too sparse to constrain the half-life of ROS to any reasonable accuracy. This Figure has to be deleted or much more data has to be provided to make a meaningful statement about ROS half-life.

p. 20, line 4: It should be explained to what “improvements” compares to. Similar instruments by other groups use some of the “improved” conditions as well. Please be precise in your statements.

p. 20. Line 21: See above. The data presented here cannot support a lifetime estimate.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-161, 2017.

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