

Interactive comment on “Application of time-of-flight aerosol mass spectrometry for the real-time measurement of particle phase organic peroxides: An online redox derivatization – aerosol mass spectrometer (ORD-AMS)” by Marcel Weloe and Thorsten Hoffmann

Anonymous Referee #2

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Referee comments for:

Weloe, M. and Hoffmann, T.: Application of time-of-flight aerosol mass spectrometry for the real-time measurement of particle phase organic peroxides: An online redox derivatization – aerosol mass spectrometer (ORD-AMS), Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2019-406>, in review, 2019.

General comments:

C1

Weloe and Hoffmann describe an online derivatization technique for the measurement of peroxides in aerosol particles in real-time using an aerosol mass spectrometer (AMS). The technique involves using the reaction of triphenylphosphine (TPP) with peroxides, generating triphenylphosphine oxide (TPPO) which is measurable by the AMS. The authors use the TPP/TPPO system to measure the particle-phase peroxides formed in secondary organic aerosol (SOA) chamber experiments of alpha- and beta-pinene ozonolysis. Peroxide concentrations are measured to increase with the onset of SOA formation, then decrease over time; however, these results are not validated with other techniques or standards. Since peroxides are thought to be important species for SOA formation and most techniques measuring peroxides require offline analysis, the real-time measurement of such species would be of great interest to the atmospheric chemistry community. Despite the potential utility of the described technique, the paper contains several large unanswered questions and deficiencies that should be addressed before publication. Unless major changes are made and additional work is done, this cannot be considered a quantitative technique (as stated in the abstract). Finally, the manuscript should be proofread for English grammar before resubmission. Scientific questions and grammatical corrections are listed below.

Specific comments:

One major question is what is the extent of reaction/derivatization between SOA and TPP? The residence time in the condenser/reaction volume is not given, but likely impacts the extent of derivatization. What tests were done to determine whether or not the aerosol was fully reacted with TPP? I do not see any mention of varying the reaction time and how this impacts the observed concentration of TPPO. At the very least, the diffusion of TPP in an organic matrix could be estimated to determine if the reaction time is long enough to get full mixing between a typical organic particle and the derivatization agent. In addition, it's possible that reaction of TPP with semisolid organic particles might be limited to the particle surface, thus limiting ability of the technique to give quantitative peroxide concentrations. Please comment on the potential effect of

C2

high viscosity/semisolid particles and their reaction with TPP.

The other major issue with the manuscript is the lack of experiments using organic peroxide standards to help determine the efficacy of the derivatization technique. While a suitable standard may be difficult to find, there are commercially available organic peroxides which could be used. Some combination of validation using standards or offline techniques to compare measured peroxide concentrations (from TPP/TPPO system) should be used to validate the technique.

The ionization efficiency of TPP and TPPO should be stated in the main text earlier, potential at the end of section 2.3 or in section 3.2.

“CSTR” needs to be defined in line 116.

How was the ozone concentration estimated (line 128)?

What is meant by “regular MS” (line 132)? Does this refer to EI-MS?

If a high resolution AMS was used, why use unit mass resolution peaks (e.g., m/z 277 for TPPO) rather than the high-resolution m/z values or identified ions?

In section 3.3, it is stated that the experiments showed a constant background contribution of TPPO from TPP; however, these values vary in the SI. What is the impact on calculated peroxide concentrations when experiment specific corrections are used?

During SOA experiments, there are periods where TPP is not added. Please describe how this is accomplished? Also, in Figure 3 (a and b), why are there gaps in the data (excluding the grey bars)? In Fig. 3b, why is the volume so variable?

In Figure 3a, what causes the increase in detected TPP when SOA is formed? Is it because there is additional surface area for the TPP to condense onto? Or is it due to some increase in collection efficiency?

In the Fig. 3 caption, the time resolution is given as 10 minutes, but the abstract says 1-2 minutes.

C3

Why use SMPS volume to quantify the SOA rather than the AMS? And why quantify peroxide concentrations in terms of volume at all, instead of mass?

It isn't clear what corrections are done to the data, if any. For example, is the data corrected for dilution in the chamber or AMS collection efficiency?

What systems were studied in the references given in lines 201 and 202 (Epstein et al. 2014, Li et al. 2016, Mertes et al. 2012)? It's not clear how these studies are related to the manuscript.

Does the formation of SOA interfere with the quantification of TPP/TPPO in the AMS mass spectra? AMS mass spectra of SOA + TPP/TPPO should be shown either in the main manuscript or the SI.

Does all of the TPPO that is formed from the SOA + TPP reaction stay in the particle phase? Any partitioning of TPPO to the gas phase would limit the quantification of peroxide.

In Figure 5, only m/z 277 looks to be bimodal, not the organic or sulfate as stated in the manuscript (line 217). I also don't find the inclusion of all of the size distribution data to be particularly useful. Some of these figures and discussion could be moved to the SI.

In line 263, ozone is excluded as a direct oxidant for TPP. This should be mentioned much earlier in the manuscript given that it is an obvious question that clouds the interpretation of the preceding results.

Technical corrections:

Line 31, remove “however”

Line 73 should read “and use this”

Line 85 “carrier gas to deliver”

Line 99 “functions as a detector”

C4

Line 100 "the beam passes"
Line 121 "was nebulized"
Line 140 "background signal has to be"
Line 191 "In any case, the"
Line 195 "As seen in"
Line 202 "Mertes and coworkers"
Line 240 "diameter depends on"
Line 253 "increased rapidly with the formation of SOA" or something to this effect
Line 258 "SOA concentration supports the concept"
Line 276 says only peroxides are detected during weekdays, but the weekend days are listed in parentheses

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