

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 #1

Received and published: 2 December 2019

Weloe and Hoffman present a new technique to measure and quantify organic peroxides in secondary organic aerosol (SOA) with the Aerodyne Aerosol Mass Spectrometer (AMS). They flow the sample (both laboratory generated and ambient SOA) through a reaction volume, where the organic peroxides in SOA react with triphenylphosphine (TPP) to form triphenylphosphine oxide (TPPO), and the AMS measures the TPPO to quantify the organic peroxides in SOA. As the AMS uses hard ionization (70 eV electron beam to ionize the gases), speciation of SOA compounds is typically limited and

challenging. This novel technique provides a way to allow the AMS to start identifying classes of compounds in SOA. Also, this provides a potentially useful method in minimizing sample handling, reducing potential experimental concerns (e.g., reactions on filters prior to sample handling). However, there are measurements and experiments that are currently missing that limits the current understanding, validity, and limits of this technique. After revising, this paper will fit into the scope of AMT and will be of great benefit for the AMS and analytical community.

Major Concerns: (1) The biggest thing missing from this paper is that the authors did not run any organic peroxide standards to investigate this technique. Running standards of a couple organic peroxides that are atomized into aerosol to investigate the percent conversion/yield of TPP to TPPO in the AMS would be beneficial in understanding the quantification. For example, when TPP is used in laboratory, it takes ~30 minutes to convert the organic peroxide to TPPO (e.g., Chiba et al., 1989; Aimanant & Ziemann, 2013). However, the authors don't discuss the reaction time/residence time, if TPP is always in excess, etc.

(2) Further, experiments that indicate the percent conversion/yield in solid vs liquid SOA and mixtures, both with known standards and amounts, is needed, to understand the quantification. As SOA can range from solid to liquid in the atmosphere and chamber studies, does the percent conversion remain constant or does it increase as the SOA becomes more liquid? Further, does the percent conversion remain constant from a purely organic peroxide atomized aerosol to a mixture of different percents of organic peroxides with other types of organics?

(3) For both experiments, showing a comparison of the AMS quantification vs another method (e.g., iodometric) (e.g., Epstein et al., 2014) would provide further confidence in the quantification of organic peroxides in the AMS through this technique (esp. since this is a new technique, a benchmark vs a well established technique is needed for further proof-of-concept and understanding of the quantification).

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(4) Are there potential reactions with other functional groups that may lead to misquantification as an organic peroxide? E.g., if there is aerosol with hydrogen peroxide (Chellmani & Suresh, 1988), which occurs in ambient air or epoxides (Sonnet & Oliver, 1976), does this lead to a positive bias in the TPP conversion to TPPO and in turn a positive bias in the amount of organic peroxides prescribed by this method?

Minor concerns: There are many grammatical issues throughout the text, making some sentences very difficult to understand. Please revise.

Check references. Some references are listed twice (e.g., Canagaratna et al., 2007; Mertes et al., 2012).

For the TPP + ROOR' \rightarrow TPPO + ROR' figure, could the authors show a more explicit arrow pushing/mechanism, as it is currently not very clear how oxygen is transferred to TPP and the organic keeps both R groups.

Line 116: What is CSTR?

Line 117: What is the residence time for the flow reactor?

Line 120 - 122: Is the ammonium sulfate seed charged and size selected?

Section 2.4: What was the RH & temperature for the experiment?

Line 186 - 187: Could you provide some examples for the reactions, instead of $A+B \rightarrow C$ and $C \rightarrow D$?

Line 197: Instead of assuming 1.2 g cm^{-3} , why did the authors not take the parameterization from O/C and H/C ratios (Kuwata et al., 2011).

For the PToF figures (Fig. 5 & 6) and starting at line 214, please include total OA with m/z 43.

As the m/z 44 vs m/z 43 triangle plot or H/C vs O/C plot has been used to signify oxidized and potentially organic peroxides (e.g., Ng et al., 2010; 2011), how does that

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appear for your experiments (colored by peroxide/SOA, for example).

References:

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