

AMT-2019-406- Reviewer Comment 1

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.

Answer: The reviewer is right, and we admit that this is a weakness of the manuscript. In fact, however, we performed experiments with several commercially available organic peroxides, e.g. lauryl peroxide or benzoyl peroxide, and the qualitative results were as expected, i.e. peroxide compounds gave a clear signal, non-peroxide compounds did not (when background correction was applied). One of the problems with the peroxide standards studied is probably related to a substantial change in volatility after the reaction with TPP, which is likely a result of the breaking of the molecules into smaller units, e.g. the formation of benzoic acid from benzoyl peroxide. The changing aerosol mass also changed the partitioning of the analytes, which made it difficult to quantitatively determine the reference compounds. In fact, the same behaviour can be expected for structurally similar R-O-O-R peroxides in the atmosphere, and it can probably be said that the method developed is semi-quantitative for such compounds. Nevertheless, it can be assumed that most peroxides in the ambient atmosphere are hydroperoxides. Although there is certainly a vapour pressure difference between the hydroperoxides and the corresponding OH functionality after the reaction with TPP (R-O-O-H → R-O-H) (Compernolle et al., 2010, Atmos. Chem. Phys.), the difference is not of several orders of magnitude as in the case of the standards used for this study. Therefore, we used the standards for the general proof of feasibility of the method and not for calibration. To make this limitation of the method clear, we have included an additional paragraph in the manuscript (section 3.1):

“ Experiments with peroxides (R-O-O-R) as reference compounds were also performed, using commercially available organic peroxides. e.g. lauryl peroxide and benzoyl peroxide. While these experiments clearly showed the formation of TPPO from TPP, the use of these compounds for quantification was not possible, since the peroxide standards studied undergo a substantial change in volatility after the reaction with TPP. Therefore, lauryl peroxide and benzoyl peroxide were used to demonstrate the general proof of feasibility of the method, however, not for calibration. “

Reaction time and concentration ratios of analytes and reactants are now also discussed and mentioned in the revised manuscript text.

(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?

Answer: Here too the reviewer has a point. SOA is a complicated matrix, and several experimental/environmental parameters can affect the results. Therefore the phase state of SOA can also influence the peroxide measurements, as discussed in the manuscript. However, the main advantage of the presented method is the high time resolution, which to our knowledge is not achieved by other techniques. Therefore, we believe that the developed method should be made

available to other researchers, although not all possible effects on the measurement results have been investigated in detail. It should also be mentioned that the relative humidity was always above 60% and the temperature between 22 and 25°C. Consequently, we expect the SOA to be liquid for all experiments performed. All aspects discussed here are now also discussed in the revised manuscript:

“Another aspect of SOA experiments which include chemistry, as in the case of peroxide-TPP reaction, that have to be considered is the question of the phase state of SOA. According to Koop et al. (2011) SOA is expected to be a liquid under the condition used for our experiments (22-25 °C, r.h. 60%). Also the AS seed particles can be expected to behave liquid-like (Matthew et al., 2008). As a consequence the diffusion time of TPP within the particles should be approximately one second (Koop et al., 2011), which is much shorter than the residence time of about 35 seconds of the aerosol in the ORD-setup (Figure 1). In conclusion, based on the agreement of the peroxide/SOA ratio at a later stage of the experiments measured in this work and the results of former studies, the estimated diffusion times and the excess of the reactant TPP to SOA, a quantitative reaction of TPP with the particle phase peroxides to TPPO can be assumed. However, in future investigations, the method should be revalidated using as aerosol particles composed of pure single component peroxides.”

(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).

The difficulty here lies in the comparability with other methods (e.g. iodometry), since here too the time resolution is completely different. Only at the end of the experimental runs, when the peroxide concentration becomes stable, such comparisons can be made. Exactly this is described in the manuscript, but not carried out by the authors themselves, but by comparison with the results of other groups who used the same chemical systems (α -, β -pinene/ozone). An additional sentence in the revised manuscript points out the detailed procedure. However, we agree with the reviewer that in future studies with the described method additional simultaneous measurements would be helpful.

(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?

The reviewer is right. Hydrogen peroxide in the particle phase would also be measured with the method presented. However, this will be the case with most peroxide measurement techniques (e.g. iodometry) and could only be avoided by a combination of enzymatic methods or the use of separation techniques (e.g. LC). In both cases the essential advantage - the high time resolution - of the presented technique would be lost. Although a clear distinction between hydrogen peroxide and organic peroxides would be desirable, a close chemical connection between the two analytes can always be expected, e.g. the hydrolysis of organic peroxides forming H₂O₂. The second reference mentioned by the reviewer (Sonnet & Oliver, 1976) investigated a different chemical system (reaction of triphenylphosphine dihalides with epoxides).

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

We have tried to fix as many errors as possible

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

Corrected

For the $\text{TPP} + \text{ROOR}' \rightarrow \text{TPPO} + \text{ROR}'$ 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.

We introduced now more information about the possible reaction mechanism and show additional reaction equations of the TPP + ROOR' reaction.

Line 116: What is CSTR?

Explained now in the text : continuous flow tank reactor

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

The values are now given in the edited manuscript: SOA-Reaktor: 13,5 min; TPP-Reaktor: 35 s

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

The AS seed particles was not dried but not size selected as described in the text.

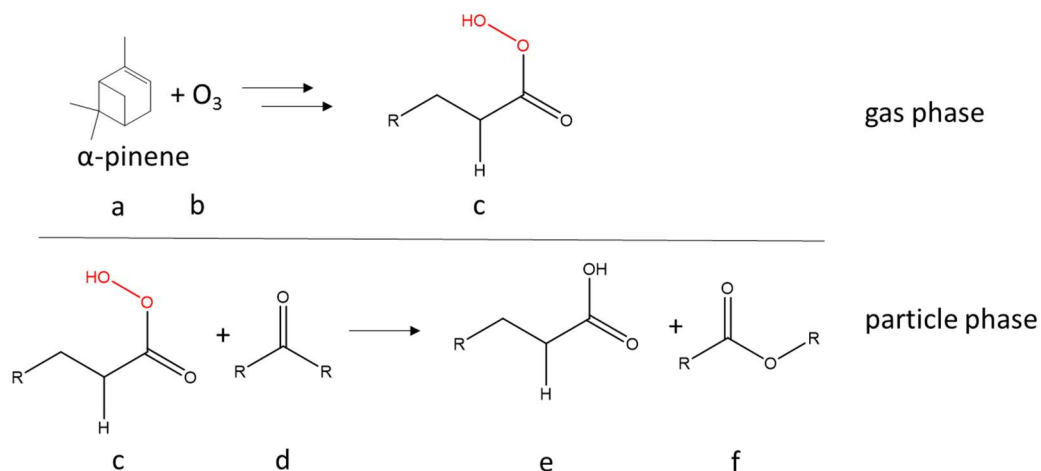
Section 2.4: What was the RH & temperature for the experiment?

These data are given in the text now.

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

Several reactions are listed now:

“.....reactions with alcohols or aldehydes forming aldehydes or carboxylic acids, or hydrolysis followed by the loss of H_2O_2 (Zhao et al., 2018; Clafin et al., 2018; Epstein et al., 2014)”



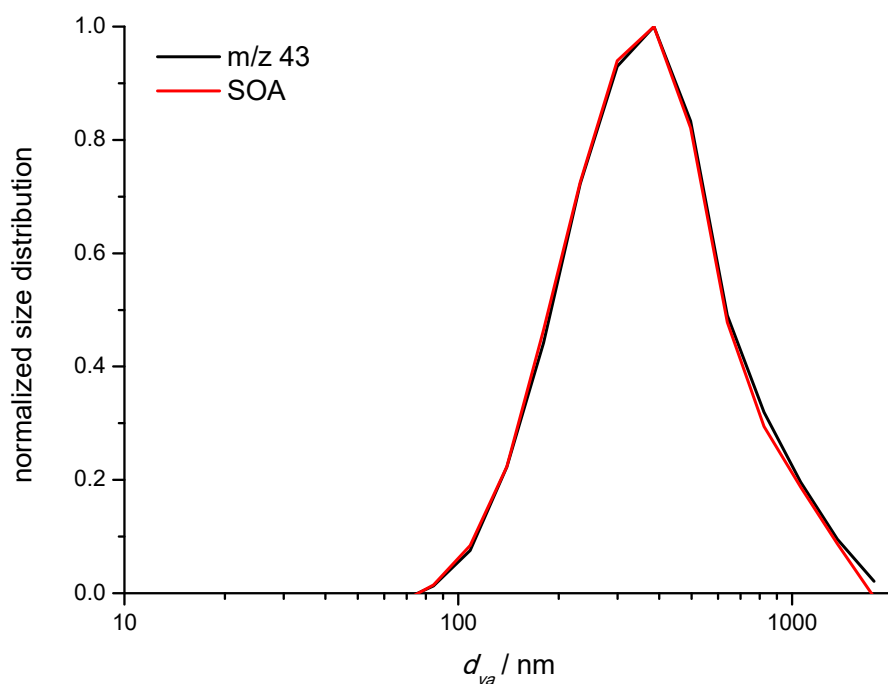
Line 197: Instead of assuming 1.2 g cm^{-3} , why did the authors not take the parameterization

from O/C and H/C ratios (Kuwata et al., 2011).

The density values are quite similar, 1.19 g/cm^3 for H:C = 1.64 and O:C = 0.41., β -pinene: 1.24 g/cm^3 for H:C = 1.47 and O:C = 0.40.

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

We could add a figure such as the figure below, indicating that m/z 43 is representative for OA. However, we are not convinced that an additional figure is necessary.



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 appear for your experiments

This is certainly an interesting point for discussion, however, beyond the scope of the manuscript. We will pick that up in the upcoming paper about the presented technique.