

Interactive comment on “Identification of Organic Hydroperoxides and Peroxy Acids Using Atmospheric Pressure Chemical Ionization – Tandem Mass Spectrometry (APCI-MS/MS): Application to Secondary Organic Aerosol” by Shouming Zhou et al.

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Zhou et al. propose a new method to detect the hydroperoxides and peroxy acids in complex matrices such as organic aerosol. This analytical method is based on atmospheric pressure chemical ionization coupled with a mass spectrometer. While this study presents a promising method, additional discussions/information are needed before the publication.

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General comments: What is the purity of the standards synthesized? It is important to know the presence of potential artifacts to better understand the MS data. NMR data would be appreciated.

Response: We reported the purities of the ROOH and other standards in the manuscript on page 3 line 1-5. As none of the ROOH standards are 100% pure, this makes the interpretation of the full scan and SIM mode mass spectra of ROOH difficult. We mentioned this point in the paper on page 4 line 23-26: “Note that we do not attempt to interpret the mass spectra of ROOH and other standards obtained under full scan and SIM modes due to the presence of stabilizers and other impurities in the standard samples that make the mass spectra complex. Instead, we focus on the protonated and ammoniated molecular ions of the ROOH molecules.” In particular, we do not feel that NMR data would enhance the paper because mass spectral data are only reported from the ROOH components of the samples, and not from the impurities.

Page 3. Lines 31-32: As the authors mentioned the hydroperoxides are thermally unstable, so did they try to optimize the temperature of the vaporizer? Does it have an effect?

Response: This question has been addressed above in our response to Reviewer 2.

Page 4. Lines 23-26: it is not clear why the authors decided to not look at the MS into more details. I can understand that in the MS without the addition of AA it is not necessarily worth it but in the presence of AA I do think it is important to have a closer look to check if other fragmentations (specific?) occurred. So the authors should dig into the MS to look at the presence of other specific fragments or clusters.

Response: As mentioned above and in the paper, the purities of the ROOH standards range between 32-80%. Therefore, without knowing the composition of stabilizers and other impurities in the ROOH standards, we do not think a full interpretation of the mass spectra of ROOH is possible nor necessary, i.e. our goal is not to analyze the full composition of the commercial samples and, instead, we focus specifically on the

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tandem mass spectrometry of the ionized ROOH compounds.

Page 5. Line 5 Please provide the product spectra and MS/MS spectra for all the standards tested. It is important to have such information.

Response: The product spectra for all the $[M+NH_4]^+$ standards tested (namely tert-butyl-hydroperoxide, 2-butanone peroxide, peracetic acid, benzoyl peroxide, di(dodecanoyl)peroxide, di-tert-butyl peroxide, erythritol, pinonic acid, and 2-nonenal) have been added into the revised manuscript into the Figure S17 and S18. As can be seen from these MS/MS spectra, only the ROOH standards produce fragments with 51 Da neutral loss.

Page 5. Lines 7-16: The authors need to provide more information on the optimization of their method. It seems that the method leads to important fragmentations of the molecular ions and the fingerprint fragment ions have generally a low intensity. Have they tried to maximize the neutral loss of 51? If the authors haven't tried to optimize this aspect, what was the reason?

Response: We optimized the CID conditions, source fragmentation voltages, and ion transfer tubing voltages, as well as the sheath gas, auxiliary gas, and sweep gas flows in order to maximize the signal from the 51 Da neutral loss products. We added this point on page 4 line 7-8 and line 11-13 of the revised manuscript.

Page 5 line 25. Similar to my previous comment, the authors need to present as much data as they can in order to demonstrate the robustness of the technique. In addition, some of the MS are quite noisy and lead to the question of the sensitivity of this analytical method. While it is promising and it seems very selective for the analyses of hydroperoxides, the results presented here indicate that it is not a sensitive method. What is the SOA mass collected from the chamber experiments? The LOD reported page 6 are very bad (\sim mg L⁻¹) compare to the current standards in the characterization of organic aerosol (\sim ng L⁻¹). The authors should discuss this issue especially in the perspective of the chemical characterization of hydroperoxides within environmen-

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tal matrices (e.g. SOA) and the instability of such products. Page 7. line 10-12 The authors claim that MS/MS will yield low detection limit and allow the identification of the hydroperoxides & peroxy acids. Based on the MS/MS spectra presented and the concentrations used in this study I don't think the authors can claim to propose a method with "a low detection limit". In addition, the authors need to report in the captions the concentrations of the solution and/or the mass of organics needed to generate the MS data.

Response: We thank the reviewer for making these points. We agree that the neutral loss of 51 Da from the ammoniated molecular ions of the ROOH standards may not lead to the most intense fragments in the ROOH product spectra. This will compromise the sensitivity of the method. Nevertheless, the purpose of this work is to illustrate a new, selective analytical method which is characteristic for ROOH products that can be used to identify/quantify ROOH in complex matrices. To specifically address the point about limit of detection (LOD), we performed additional experiments to determine the LOD of cumene hydroperoxide by applying selective reaction monitoring (SRM, m/z 170 > m/z 119) in the LC-MS/MS analysis. The chromatogram and the calibration curve are presented in Figure S12. As expected, the LOD is much lower: i.e. 0.9 μ M, more than 300 times lower than with the direct infusion experiments. This confirms our expectation that MS/MS analysis coupled to liquid chromatography can lower the LOD in ROOH analysis. We added this argument on page 5 line 23-24.

Page 7. Lines 14-16 The authors should propose similar Figure as Figure 5 for the SOA generated under humid conditions. The authors have to be prudent in their conclusions and keep in mind the high reactivity of oligomeric products formed from the reaction of Criegee radicals with protic substances (e.g. Riva et al., 2017 Atmos Environ). Indeed, such species can have been degraded during the 72 hours of sampling and/or throughout the analytical protocol. Did the authors estimate the degradation of the hydroperoxides/peracid?

Response: As we mentioned in the manuscript, the mass spectrum of SOA formed

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under humid conditions (RH=50%) is extremely similar to that under dry conditions (RH<5%) and so we do not think it is necessary to present it in the paper, but it is in the SI (Figure SI11). We added the following sentences on page 6 line 33 to page 7 line 2 of the revised manuscript to address the reviewer's comment: "As well, while the ROOH formed under dry and humid conditions show similar mass spectra (Figures SI11), we note that more α -hydroxy hydroperoxides may be formed under humid conditions as a result of Criegee reactions with water, which may decompose during the ionization processes due to their thermal instability". This might be the cause of the similar mass spectral patterns.

Technical comments: m/z should be in italic.

Response: This has been changed.

Page 6. Proper references for the formation of dimers: Crouse et al 2013 and Ehn et al. 2014.

Response: These two references have been cited in the revised manuscript.

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