Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2017-400-RC1, 2018

Atmospheric Measurement Techniques Discussions

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.

Anonymous Referee #3

Received and published: 2 February 2018

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.

General comments: What is the purity of the standards synthesized? It is important to

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know the presence of potential artifacts to better understand the MS data. NMR data would be appreciated.

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?

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.

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.

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?

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 environmental 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.

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?

Technical comments: m/z should be in italic.

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

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-400, 2018.

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