

Interactive comment on “A quantification method for methylglyoxal oligomers and its application on 1,3,5- trimethylbenzene SOA” by Maria Rodigast et al.

Anonymous Referee #2

Received and published: 11 November 2016

Overall Comment and Recommendation:

This study is primarily a method development study aimed at quantifying oligomers derived from multiphase chemistry of methylglyoxal by using GC/MS with prior derivatization. Many groups have shown that when you heat certain SOA types, such as IEPOX-derived SOA, you measure monomeric products (like 2-methyltetrols) in high quantities (Lopez-Hilfiker et al., 2016, ES&T). This is important since monomeric products like 2-methyltetrols are too volatile to exist in such large quantities to explain the observed SOA formation in lab or field studies. The present study utilized GC/MS with PFBHA derivatization to detect methylglyoxal monomers found in 1,3,5-TMB derived SOA. The authors systematically examined the influence of heating time, pH, and heat-

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ing temperature on the decomposition of methylglyoxal oligomers. The authors found that the best result was likely achieved when heating the extracts for 24 hours at 100 degrees C and at pH of 1. The authors found that the oligomers accounted for up to 8% of the total SOA mass.

The method the authors develop could be very useful in trying to provide mass closure of the oligomer fraction of methylglyoxal-derived oligomers. More importantly, this method could likely be adapted to determine oligomer mass fractions in other types of SOA. This is important since we currently lack appropriate authentic standards to quantify the oligomer content of the SOA. More often we have standards available to quantify the monomers, so this method would be of interest to many research groups working in this area. Before I can recommend final publication in ACP, I have many specific comments that need to be addressed by the authors. These specific comments are outlined below. Due to the nature of these comments, I must recommend to the Editor that this manuscript be accepted with major revisions noted. There are several method details missing that need to be clarified or added to the main text. In addition, in several sections of the manuscript, the English writing is at times quite poor. As a result, I encourage the authors to conduct further editing on the writing before resubmission.

Specific Comments:

1.) Citations in main text:

The authors cite references through the manuscript using "Last name of first author et al., Year." As an example, please refer to Page 2, Line 52. The the authors should change to Kalberer et al. (2004). The style in ACP is always "Author last name et al. (year)."

2.) Filter Extractions:

Have the authors tested extracting the filters in an organic solvent such as acetonitrile

or methanol? I wonder how the extraction efficiencies of potentially large oligomers change with extraction solvent? This factor should at least be discussed in this manuscript and the likely uncertainties in obtaining exact oligomer concentrations from this method. What I'm getting at is the authors assume in the text that the filter extraction efficiency is likely 100% in water.

3.) GC/MS operating details:

You should state here explicitly how long your GC/MS run is. Since it appears this is a long GC/MS run, did the authors check to see how the methylglyoxal standard calibration changes throughout the run? For example, did the authors consider re-running the calibration at the end of the run? Did the response factor change/drift dramatically?

4.) Method Development:

In the method development section when varying heating time, pH, and heating temperature, it seems that for the latter two the same experiment was used (i.e., experiment 2). In contrast, the heating time was explored with experiment 3. I think the authors would have been better to use the same type of aerosol generated under the exact same conditions when exploring these parameters of the method. I'm curious to know why this wasn't done or why it is justified to do this as is?

5.) SOA Yields:

Since the authors spend time in this study reporting SOA yields from 1,3,5-TMB oxidation, I have some questions about the differences in the amount of organic aerosol produced under the different RH conditions. Considering that you observe more SOA under dry conditions when compared to more humid conditions, I wonder what role your chamber walls are playing? Recent work from the Caltech (Seinfeld), CU-Boulder (Jimenez and Ziemann), and CMU (Donahue) groups suggest that the wall effect could be really important, especially if your goal is to report SOA yields in the literature. Thus,

maybe you are losing more things to your wall under higher RH conditions? Have the authors considered how to correct SOA yields for this effect? If not, you should at least acknowledge the likely importance of wall losses of semivolatile and less volatile organic vapors.

6.) Page 9, Lines 298-299:

Could it be that methylglyoxal's chamber wall losses are also changing with RH? Did the authors consider injecting methylglyoxal in the gas phase of the chamber and investigate its wall losses with different RHs? That might provide more insights into the importance of your chamber wall.

7.) Page 9, Lines 329-332:

I wonder how the different seed aerosols you use might cause differences in aerosol phase separation/morphology? What role could this potentially have in explaining the differences in the oligomer fraction?

8.) Oligomer Types:

It appears that the authors only consider the oligomer type resulting from methylglyoxal + methylglyoxal type reactions. However, considering the plethora of other monomers when oxidizing a VOC like 1,3,5-TMB, why did the authors not consider other types of oligomer reactions involving methylglyoxal + some other oxidized product? Was there no evidence for this in your GC/MS data? Related to this, why didn't the authors provide a TIC or EIC in the main text? In either the TIC or EIC, it would be helpful to provide peak labels and likely respective mass spectra to each chromatographic peak.

I mention this as recent work by Lin et al. (2014, ES&T) demonstrated the varying types of IEPOX-derived oligomers under different RH and seed aerosol conditions. It appeared from their LC/MS data that there was a very wide degree of types (e.g., light-versus non-light absorbing) and lengths of oligomers present.

Minor Comments:

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1.) Introduction, Lines 36-42: When generalizing the oligomeric mechanisms leading to SOA, why not include those derived from acid-catalyzed hydrolysis of epoxides (e.g., Paulot et al., 2009, Science, Surratt et al., 2010, PNAS; Lin et al., 2014, ES&T)?

2.) Page 2, Line 46. You should probably define the ESI/MS/MS acronym being associated with tandem mass spectrometry interfaced to ESI.

3.) Page 2, Line 50:

Probably change "the effort for structure" to "past efforts for structural"

4.) Page 3, Line 72:

Do you mean to say "fundamental" here instead of "foundation"?

5.) Page 3, Line 87:

should this say instead: "was investigated in the Leipziger AerosolKammer (LEAK) chamber"?

6.) Page 3, Line 90:

Maybe change "ammonium hydrogensulfate" to "ammonium bisulfate"

7.) Page 3, Line 90:

Maybe change "ammoniumsulfate" to "ammonium sulfate"?

8.) Page 4, Line 92:

Add vendor and model to "(PTR-TOF MS)"

9.) Page 4, Line 99:

Add vendor and model to "(SMPS)"

10.) Page 4, Line 99:

Why do the authors use 1 g cm⁻³ density? Are you using this based on a previous

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study? If so, please justify why you used this aerosol density.

11.) Page 4, Line 100:

Change "the particle phase" to "aerosol"

12.) Page 4, Line 100:

Insert comma between "experiments" and "1.2"

13.) Page 4, Line 104:

Did the authors determine what the break through could be on these filters during experiments? Were control tests done to know how well the denuder worked?

14.) Page 7, Line 252:

Change "condensate" to "condense"

15.) Page 8, Lines 279-281:

Citation is needed here. Are the authors arguing that particle-phase acidity might also be required for methylglyoxal oligomers to form? If so, is this why you think LWC matters? That is, the higher the LWC the more likely the aerosol pH is less acidic and thus affecting the amount of SOA due to oligomer formation? This is unclear to me in the current text.

16.) Page 9, Line 308:

Do the authors mean to say "on average $\sim 2\%$ "?

17.) Page 10, Line 350:

Change "increases" to "increase"

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-574, 2016.

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