**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 #1**

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**General Comments**

This manuscript describes the careful optimization of a method designed to thermally break down methylglyoxal oligomers and detect them as derivatized monomers. Such a method is a welcome addition to the experimental toolbox of aerosol chemists. Overall, the methods and data are clearly explained and the conclusions are reasoned out logically. While the optimization process and results are completely valid, the authors’ ability to interpret their work is limited by the fact that standards for methylglyoxal oligomers do not exist. To be more precise, the authors have not demonstrated that the maximum amount of oligomers that they have been able to break down and detect is equal to the total amount of methylglyoxal oligomers in their samples. However, the manuscript seems to assert this questionable assumption many times. In fact, as the authors point out at the end, the 5 – 10-fold difference between methylglyoxal oligomers detected in this study and total oligomers detected by different methods in other studies of the same system suggests that many other oligomers are present, but don’t either don’t break down at all, or don’t break down into monomers that were detectable using the present method. However, the lack of detection of any other carbonyl compounds mentioned in this study suggests to this reviewer that the undetected oligomers are most likely some type of methylglyoxal oligomer that is irreversibly formed. It may be that methylglyoxal acetal oligomers break down to monomers with heat (as is the case for glyoxal), but methylglyoxal aldot oligomers do not. Until there are methylglyoxal oligomer standards of each type to test, this question is not likely to be answered definitively. To address this issue, the authors should qualify all of their statements (including even the title) about what they are detecting, perhaps by replacing “methylglyoxal oligomers” with a more exact phrase such as “reversibly-formed methylglyoxal oligomers.”

This work will be of interest to those who study the chemistry of organic aerosol particles in the lab and in the field.

**Specific Comments**

**Line 19:** Some qualifying phrase seems to be missing here. Is this percentage the fraction of anthropogenic emissions, or of non-methane hydrocarbon emissions? Are aromatic emissions in China really 52% of the total of all biogenic and anthropogenic hydrocarbon emissions, including methane?

**Line 92:** It would be helpful to readers if a 1-sentence summary could be included here about how O3 + TME generates OH radicals and why this OH source was chosen.

**Line 96:** Are the deliquescence and efflorescence RH values known for either seed particle material? Perhaps the phase of these particles is relevant to the results.
Line 99: Is the choice of organic aerosol density (1 g/mL) based on a literature measurement?

Line 102: What absorbent material were the denuders coated with?

Line 191: There is unclear logic here. If the incompletely derivatized methylglyoxal is able to reform oligomers once the temperature drops to 298 at t = 15 h, wouldn’t the yellow bar in Figure 1b be even smaller than the black bar?

Line 195: This paragraph is confusing. The authors suggest a possible explanation, then seem to eliminate it in the next sentence (assuming that “decomposition” and “loss” are the same process), without offering an alternative explanation.

Line 215: The manuscript states here that Rodigast et al. 2015 found no influence of the pH on the PFBHA derivatisation reaction. However, in line 201 the same study is cited in support of an optimal pH value of 1 for the reaction. How can a factor with no influence be optimized?

Line 232: This is an important statement, but it leaves the reader wondering which other carbonyl compounds were being monitored in this work. It would be very helpful if the authors would list these compounds.

Line 236: Confusing statement. According to Table 3, the method was developed using filters from experiments 2 and 3 from laboratory 1,3,5-TMB oxidation studies (plus methylglyoxal monomer standards). Now the method is applied to more of the samples from the same set of studies.

Line 257: From the information given it is hard to see how these two studies “are in good agreement” with the present study, since the present study is measuring no acidity effect while the two literature studies compared seed / no seed conditions.

Line 289: The authors’ measurements of the percentage methylglyoxal in 1,3,5-TMB SOA are right in line with other published values. Did Healy et al and Cocker et al. use seed particles? Can the authors comment on whether such percentages are consistent with partitioning theory and the vapor pressure of methylglyoxal?

Line 301: Do these literature studies suggest that either of the two explanations offered in the previous sentence are more likely than the other?

Line 315: The phrase “opposite trend” was unclear. What trend is this trend the opposite of?

Line 334: Doesn’t this logic also apply to the next two reactions that involve water loss? I am unsure why aldol reactions are enhanced and esterification and imidazole formation are decreased at high RH, when all involve water loss as part of the mechanism.

Technical Corrections

Line 194: “might be” should be “are”. The authors know that H+ and NH4+ ions are present in the samples and therefore the aqueous extracts.

Line 205: “PFTFE” should be “PTFE”

Line 253: “condensate” should be “condense”

Line 314: The period is missing after “conditions”

Line 343: “is” should be “it”

Line 352: “increases” should be “increase”

Table 6 does not provide any additional information beyond Figure 5b, and could be eliminated.

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