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Comment

# ***Interactive comment on “A smog chamber comparison of a microfluidic derivatization measurement of gas-phase glyoxal and methylglyoxal with other analytical techniques” by X. Pang et al.***

**Anonymous Referee #2**

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This paper presents a promising approach for measuring atmospheric glyoxal and methyl glyoxal based on an automated system for generating derivatives ready to be injected into a gas chromatograph. Because the study of atmospheric dicarbonyls remains data limited this is an important contribution. Overall the paper gives a good description of the method and presents the results for specifying the optimal analytical conditions.

I recommend publication pending some minor revision to clarify a few points and give

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a better sense of the precision. Furthermore, there needs to be a more thorough analysis of the single photolysis run that compared the microfluidic derivatization method to other measurement approaches. What is the meaning of the outlier points where microfluidic derivatization disagrees with the other methods?

————— specific comments —————

page 5758; Its a minor point, but be careful not to oversell this method as being simpler than optical approaches. Whether a technique is simple and straightforward depends on what you are familiar with. To a spectroscopist derivitization and GC-MS will seem incredibly complex, prone to interference and dependent on too many moving parts. You can let this method stand on its merits without having to judge other methods. Comparing the relative sensitivities and measurement frequency among methods is reasonable, but leave it to the reader to decide what is simple versus complicated.

page 5765 The assertion that a liquid-based calibration approach using pure carbonyl-derivatives needs further discussion. Using this as a calibration approach fails to verify that the reaction efficiency is 100% or that the enrichment ratio is constant. Further, it cannot evaluate whether there are any inlet losses. Perhaps this approach can be a component of a calibration scheme, but there also will need to be some evaluation of sampling efficiency and verification of the enrichment and conversion efficiency.

Page 5766 Please say something about the volume of sample collected and the length of time for each sample. Is the air sample time short relative to the 30-minute frequency or does each measurement represent an integration over the 30-minute interval? I could not find a specific mention of this detail in the text.

page 5774 The comparison of microfluidic derivatization to other methods warrants a fuller discussion. It appears that the other methods and the model simulation all have a similar shape for the evolution of GLY and especially MGLY, but the microfluidic method has a few outliers that show concentrations increasing when the other methods are already dropping. It would help to present the data in a way that highlighted what

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is similar and what is different among the methods rather than treating them each separately. Would the figure still be comprehensible to make two larger panels (one each for GLY and MGLY) showing all the measurements simultaneously. With just one experimental run it is hard to know if the outliers are just an analytical glitch, or if the method is responding to some artifact. A comparison to the other methods ought to include some measure of how well they compared that is more quantitative than just stating that they compare reasonably well. Does the new method agree better or worse to the other methods than they do to each other? Perhaps a table showing the pairwise correlations or estimates of bias and offset would be useful here. The problem of comparing continuous measurements to finite grab samples will need to be considered.

page 5776, I think it is overstating things a bit to call the microfluidic method 'rapid' if the sample frequency is only 1/30 minutes. I see that the sample preparation is rapid compared to manual approaches for preparing carbonyl derivatives - the statement here could make a clearer distinction between rapid sample preparation and rapid sample collection, along with some comment about the need for continuous measurement versus finite sampling or long-duration integrated sampling.

Figure 6 or associated text, the calibration curves need to include uncertainties for the coefficients. The uncertainty will guide choice of how many significant digits to include. I doubt that the coefficients are as precise as implied by presenting them to 6 digits.

Figure 8, the uncertainty of the slopes needs to be presented. Is the intercept truly indistinguishable from zero?

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Interactive comment on Atmos. Meas. Tech. Discuss., 6, 5751, 2013.

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