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Atmospheric Measurement Techniques Discussions

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 #1

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The manuscript describes a powerful extension and combination of existing methods by combining PFBHA derivatization on a microfluidic device with GC-MS. The target molecules discussed in this work are glyoxal and methylglyoxal, two molecules of increasing importance. The manuscript also describes intercomparison with other techniques and shows generally good agreement with these other methods. The work pursues an important direction, as there is a strong need for new, cheaper, and easier to use techniques for measurement of these two important molecules. The method appears to have better detection limits than SPME, which represents a real advance

although the time-resolution is slower than that of some of the competing, but complex, methods, e.g., CE-DOAS, BBCEAS, LPI. The subject is well suited to AMT and timely. I however have some comments that should be addressed before publication in AMT.

I) My first comment is that some of the authors have published a manuscript in the Journal of Chromatography A (Pang et al. 2013) and that publication has a lot of overlap with the one under review here. The manuscript was available online May 8 of this year, before the manuscript discussed here was accepted for publication in AMTD. The manuscript under review here is referenced in the published one as "in press". However, unless I missed this, the published one is not referenced as "in press" in this manuscript or mentioned. This situation is confusing and needs clarification for the following reasons:

Figure 1 in this manuscript is virtually the same as the combination of figures 1 and 2 in the published work

Figure 3 in this manuscript is nearly identical to figure 5 in the published work. However, in the current paper k-2 exists. I assume the difference results from the focus on glyoxal and methylglyoxal (although both show glyoxal), but an explanation would he helpful.

Figure 4 in this work is fully identical to figure 5 in the published work (copyright?).

Figure 7a is virtually identical to figure 7 in the published work.

The above highlights the strong overlap between the manuscripts.

The separation of material between the two manuscripts and thus the scientific focus of the manuscripts is a little unclear to me. The published one is framed as a method description and the one under review here is aimed as an intercomparison (as clearly stated in the title). However, the separation is fuzzy and important method development aspects are not included in the published manuscript but rather in this one, e.g., temperature optimization and more, and some of the material appear in both, e.g., some of the inter comparison.

In my opinion, it would be very helpful for the reviewers if the authors provide a rational for the approach they have taken with respect to separation of material between the two manuscripts.

II) A second major comment is that the manuscript could benefit from stating more clearly the suitability of the method for ambient measurements, especially for methylglyoxal, for which there is a strong need for better field measurement methods, and clarify the comparison with other methods, especially with respect to how “rapid” the measurements are.

1. The abstract mentions MDLs but does not mention precision or accuracy of the method nor the measurement time and whether this enables field measurements. It is stated in the abstract that “These MDLs are below or close to typical concentrations in clean ambient air.” Is this sufficient for field measurements? It is briefly stated later (p. 5776) in the manuscript that “Some further refinement of the microfluidic technique” will be necessary, but I think a clearer statement is needed in the abstract.

2. Methods, such as CE-DOAS, BBCEAS, and LIP, have better detection limits and at a much higher time resolution, if I understand the manuscript correctly. In my opinion the lower time resolution has to be discussed in detail. How does this affect the suitability for field measurements. Is 30 minutes, the measurement time, if I understand correctly, really rapid, as stated on p. 5759? A clarification is needed on the meaning of “rapid”. What is the impact of having a continuous measurement producing, e.g., 1 minute data, and one that provides a 10 minute observation (I was not quite clear on the actual sampling time used for this instrument) every half hour. The method described here benefits from simplicity and cost, but the measurement time aspect could be a disadvantage and I was surprised not to see differences in measurement times clearly addressed.

3. In an extension of above: The detection limits of CE-DOAS, BBCEAS and LIP, I believe, are achieved in a shorter sampling time than half an hour. It would be very

helpful to clearly state for how long the instrument discussed here samples compared to other instruments. If I understand correctly most of the measurement time is the GC? Also, I was not quite clear on the sampling time of BBCEAS (detection limit is quoted for 10s). For an instrument intercomparison this information is needed.

4. Some of the spectroscopic techniques can have lower detection limits if averaged to longer measurement times, depending on Allan variance analysis etc. The measurement time could be added to table 2 and whether precision and MLD improve with longer measurement time (limited, e.g., by Allan variance analysis).

4. Figure 8 shows two data sets. There are no error bars on the low concentration glyoxal measurements. Is that correct? Is it possible to show a time trace of measurements at constant low glyoxal? That would help convince of the detection limit as no zeroing experiment of the new method is shown. More directly, it would be very helpful to add a lower concentration point, e.g., blank/zeroing to figure 8.

III) Less important comments:

1. Abstract: line 19-25: “Good and less good”: needs to be more quantitative for an intercomparison paper.

2. p. 5758: Second paragraph. The detection limits, accuracies, precisions and sampling times of these methods need to be mentioned. The mentioned previous PFBHA techniques are being improved upon in this manuscript so a detailed comparison with these is helpful. How does the time resolution of ca. 30 minutes p. 5759 line 12 compare with the previous PFBHA techniques.

3. For the intercomparison: It would be helpful to clearly state how data was selected for the intercomparison. Was data from other instruments binned to the sampling time of the instrument described here (in contrast to measurement time), and how was this achieved, e.g., for SPME or FTIR.

4. p. 5774: The model results require more detail. What was the integration time, how

was it initialized, was the direct glyoxal yield from isoprene of Volkamer et al. 2006 and Galloway et al. 2011 included, were any parameters constrained to measurement, e.g., photolysis, isoprene?

Minor comments:

Line 27 and following: This is based on models. In addition, satellite observations indicate a strong missing source (e.g., Vrekoussis et al. 2009, Myriokefalitakis et al. 2008, Lerot et al. 2010).

p. 5755: Line 19 Henry et al. is an odd reference in this context, as the paper was largely instrumental. Citing a modelling study would be much better.

p. 5757 Line 1: “specialized” instead of “specialist” I think.

p. 5757 Line 18 and following. And satellite measurements are usually only available for one time of the day.

p. 5763 Feierabend et al. is using previously developed methods. Please use the ones in prior work.

p. 5773: line 14 “blank sample” It would be helpful to the readers, whether this was chamber air with no carbonyls or zero air from a tank/generator.

Figure 8: I think “FTIR” is mentioned once rather than “microfluidic”in the caption

Table 2 lists that MDLs are 3 times standard deviation of the S/N of the blank sample chromatograph. However, many methods do not have a chromatograph.

p. 7574 line 19 and following: Washenfelder et al. 2011 have reported values in Los Angeles that are well below 1 ppb as well and this work should be added to the list of manuscripts. DiGangi et al. 2012 show rural glyoxal and this could also be added as a reference.

Also p. 5754: Line 19 and following: For which manuscript is the 1820ppt value, or is it

the one from Volkamer quoted later?

References:

Volkamer, R., Barnes, I., Platt, U., Molina, L. T., and Molina, M. J.: Remote sensing of glyoxal by differential optical absorption spectroscopy (DOAS): Advancements in simulation chamber and field experiments, in: Environmental Simulation Chambers: Application to Atmospheric Chemical Processes, Springer, Dordrecht, Netherlands, 2006.

Pang et al., Microfluidic lab-on-a-chip derivatization for gaseous carbonyl analysis, Journal of Chromatography A, 1296, 93– 103, 2013.

Lerot, C., Stavrakou, T., De Smedt, I., Muller, J.-F. and Van Roozendael, M., Atmos. Chem. Phys., 10, 12059–12072, doi:10.5194/acp-10-12059-2010, 2010 Vrekoussis, M., Wittrock, F., Richter, A., and Burrows, J. P.: GOME-2 observations of oxygenated VOCs: what can we learn from the ratio glyoxal to formaldehyde on a global scale? Atmos. Chem. Phys., 10, 10145–10160, doi:10.5194/acp-10- 10145-2010, 2010.

Myriokefalitakis, S., Vrekoussis, M., Tsigaridis, K., Wittrock, F., Richter, A., Bruhl, C., Volkamer, R., Burrows, J. P., and Kanakidou, M.: The influence of natural and anthropogenic secondary sources on the glyoxal global distribution, Atmos. Chem. Phys., 8, 4965–4981, doi:10.5194/acp-8-4965-2008, 2008.

Galloway et al. Atmos. Chem. Phys., 11, 10779–10790, 2011.

Washenfelder et al. JGR, 2011, D21, DOI: 10.1029/2011JD016314.

DiGangi et al. ACP, 12, 9529 (2012), doi:10.5194/acp-12-9529-2012.

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