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Interactive comment on “Fast two-dimensional GC-MS with thermal extraction for anhydro-sugars in fine aerosols” by Y. Ma et al.

Y. Ma et al.

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Response to anonymous referee #1

Response to comment 1: It is now mentioned in Section 2.1 of the manuscript that methanol was used to dissolve the target and internal standard compounds. In this study, the LOD is determined from filters spiked with standard compounds dissolved in methanol. The LODs were determined using 1 μL injections of solutions containing 25 $\text{ng}/\mu\text{L}$ MAN and GAL and 1 $\text{ng}/\mu\text{L}$ LG. This is now given in Section 3.1. With these changes, one can readily determine the compound mass present on the filter. The use of $\text{ng}/\mu\text{L}$ units are consistent with the LOD experiments conducted here and more comparable to other published studies focused on LG analysis. It is interesting that our method appears to be approximately a factor of two less sensitive than GC-MS,

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for example, owing to the longer path length over which the analytes must travel prior to entering the GC-MS system. However, we are quite aware that the “whole PM-sampling” approach to TE more than makes up for this apparent difference. This point is alluded to in Section 3.3.3, where the concept of “effective” sensitivity is discussed.

Response to comment 2: The influence of the biomass burning matrix on the recovery of the anhydro-sugars was not conducted as part of this study. However, our research group did publish an earlier study (R. Lavrich and M.D. Hays, *Analytical Chemistry*, 2007, 79 (10), pp 3635–3645) that looked at the effect of the biomass burning aerosol matrix on the TE-GC-MS quantification of organic compounds. From this, it was generally concluded that biomass burning aerosol was not as adsorptive as diesel exhaust particles. A result which was likely due to the relatively high elemental carbon fraction in the diesel particles examined.

Response to comment 3: Normally, as is the case for MAN and GAL, we use $y = a + bx$ because it provides an indication of calibration bias. For LG, a linear fit with $y = a + bx$ indicated a slightly positive intercept. This suggested that the method responded for LG at a concentration of zero; an erroneous suggestion based on our blank tests. To compensate, we used $y = bx$ for LG. Calculation of the LG concentration using both $y = a + bx$ and $y = bx$ showed a difference of 5.7% at 150–200 ng of LG, a typical concentration in biomass burning aerosol. This difference is well within the method variability.

Response to comment 4: The data in Figure 3 were originally fit using the OLS method. Figure 3 was revised to account for the fact that the X and Y variables both contain error. The figure now shows the results of a reduced major axis linear regression as described in Ayers 2001. A slight change in the slope and y-intercept are observed. However, the overall conclusions with respect to the slight negative bias are still applicable. The Figure 3 caption and text in Section 3.2.2 were changed to better describe this revised approach to the linear regression.

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Ayers, G. P. Comment on regression analysis of air quality data. *Atmospheric Environment* 2002, 35, 2432-2425.

Response to comment 5: This is a valid point. The authors have revised the discussion in the manuscript, clarifying that the throughput advantage TE offers is only potential and depends on several factors. We now state that: Contingent on the number of samples, and sample preparation and analysis times, the TE-GC-GC-MS method affords up to an approximately two-fold increase in laboratory throughput over most currently available methods that speciate LG in aerosols. Of course, as the ability to perform batch solvent extractions in parallel increases, the throughput advantage of TE may lessen depending on the exact instrumental approach being taken.

Response to comment 6: The revised manuscript now states that the liquid extract is typically 250 μL or more for GC-MS methods. Changes due to comment 1 should also aid the reader in determining the sensitivity of the TE-GC-GC-MS method with regard to aerosols mass. To place TE-GC-GC-MS method sensitivity for LG in the proper context, it must be compared to the published sensitivity of other methods. For comparison purposes, the authors explored the possibility of reporting sensitivity for all methods as a function of total extracted and injected analyte or aerosol mass because TE is a “whole-sampling” method. However, close scrutiny of the literature revealed that many of the studies being compared did not always provide the total aerosol mass or total LG extracted, injection volume, or final concentrated volume values needed to perform the conversion. Units of $\text{ng}/\mu\text{L}$ or similar were most frequently available; thus, in an effort to be consistent, LOD values are reported for all studies, including the present one, as $\text{ng}/\mu\text{L}$. Words to this effect were added to Section 3.3.3. These should help explain why the data are presented in the manuscript this particular way.

Response to comment 7: Addition of more studies of this kind may be better for a comprehensive review paper, considering that the objective of this particular study was to develop a novel method for fast analysis of anhydro-sugars. The manuscript references more than 50 studies that in some way cover the topic of anhydro-sugars. This is a high

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reference count for a research effort (according to an internal review). Roughly 35 of the 50 references are assigned to Figure 4, which is given to compare this study's results to LG concentrations (i) in source emissions and atmospheric aerosols collected world-wide and (ii) determined using different analytical methods.

Response to comment 8: To be consistent, the sample storage temperature is changed to -50 C in the text. The freezer set temperature is -50 C, and it may vary between -45 and -50 C.

Response to comment 9: PDA stands for photodiode array, which is noted in the text.

Response to comment 10: The volume was 1 μL , and is now reflected in the text.

Response to comment 11: Wheat straw sample was sampled on 47mm diameter quartz fiber filters; PMT, CNF, and KSV samples were sampled on 67mm quartz fiber filters; all other samples were collected on 8"x 10" quartz fiber filters of 432 μm thickness from Pallflex[®], Pall Corporation. These details were added to the manuscript.

Response to comment 11: Typo was fixed as suggested.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 153, 2010.

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