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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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General comments: Ma et al present a carefully tested new method for measurement of anhydrosugars in atmospheric aerosols. The thermal extraction 2D-GC/MS method is novel and demonstrated to provide accurate and precise results comparable to those obtained by traditional methods. The work is of high quality and the manuscript clearly written. I have only a few comments that should be addressed prior to accepting the manuscript for publication. My main concern is with regard to the presentation of method LOD.

Specific comments:

1. My main concern is the presentation of method limits of detection (LOD) as solution concentrations. The method is applied to filter samples directly. The LOD values are presented based (as far as I can tell from the manuscript description) on concentrations

of standard mixtures applied to quartz filters. The solvent in the standard solutions is not specified. More important, the authors do not indicate the volume of each standard applied to test filters for LOD determination. They do indicate 100 ng of standard were applied for method recovery tests. Because the method is ultimately mass sensitive, the LOD values should be presented as masses (standard liquid concentration * applied standard volume) and not as solution concentrations (ng/μl). The LOD determined in ng/μl will depend on the rather arbitrary choice of applied standard volume and really says nothing about the sensitivity for direct TE filter sample analysis.

2. Do the authors have any insight into whether method recovery depends on the sample matrix? It appears recovery tests were performed solely on spiked blank filters.

3. Figure 1. Why was the LG calibration fit intercept forced to zero while intercepts were calculated for Man and Gal?

4. Section 3.2.2 and Fig. 3. How was the linear best fit line determined here? Since there is error in the independent variable (SE LG/PM2.5), an ordinary least squares fit will yield a slope that is biased low. OLS assumes there is no measurement uncertainty in the independent (x) variable. A more robust regression method is needed when uncertainty is present in both the independent and dependent variables. This slope bias can partly explain why the determined slope is less than 1 and less than the average ratio of 0.96 in the dataset.

5. Section 3.3.1. Because aqueous sample extraction is generally performed in parallel on a sample batch, LC sample throughput is primarily limited by analytical time and not by the sum of sample prep and analysis times (unless one divides sample batch prep time by number of samples in the batch) as implied in the discussion here.

6. Section 3.3.3. It is unclear why the liquid sample extract volume is assumed to be 250 μl for other methods. More important, a comparison of aqueous method detection limits doesn't really tell the reader much about relative method sensitivity for analysis of actual aerosol samples. As discussed above, the TE method presented here depends

on extracted mass. For other methods, sensitivity is really a function of the product of the minimum extract concentration that can be detected and the method extraction volume. As the authors point out, many other methods only analyze a small fraction of the extracted filter mass.

7. It would be worthwhile to expand the comparison in Fig. 4 of literature-reported LG concentrations to include more published studies.

Technical issues:

8. Various values (between -40 and -50 C) are specified at different points in the manuscript for sample storage temperature. It would be better to be consistent in stating this value (or range).

9. Section 3.2.1. Should IEC-HPLC-PDA be IEC-HPLC-PAD?

10. Section 3.1. What was the volume of 100 ng/μl standard applied to filters to determine method precision?

11. Please specify details about quartz filter type used in the study.

12. Fig. 4 caption, line 3: change "top the of the box" to "top of the box"

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