Atmos. Chem. Phys. Discuss., 10, C1297–C1303, 2010
www.atmos-chem-phys-discuss.net/10/C1297/2010/

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.

Y. Ma et al.

hays.michael@epa.gov

Received and published: 6 April 2010

Overview of the manuscript: This manuscript presents a very interesting and potentially robust method for fast analysis of important molecular marker compounds for biomass combustion emissions. The authors have done an excellent job of describing the method details and present preliminary data that the method serves its purpose. Although method details were given in detail in a previous paper by some of these authors (Ma and Hays, J. Chrom. A, 2008), thus this paper is limited in its method application. There are only three analytes presented here with a maximum of 8 samples analyzed. My primary concern with this manuscript is that the number of samples that have been analyzed by this "fast" method is very low. Thus the statistical evaluation of the method performance is not convincing. Next, an implicit concern related to this

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

work, is the method's potential for application with regard to widespread use.

Response: The eight aerosol samples examined in the present study are representative of primary biomass burning emissions, near-fire emissions (with atmospheric dilution), and African and U.S. ambient aerosols from contrasting polluted urban and relatively clean agricultural regions. Moreover, the study has examined biomass from forest and agricultural environments that disproportionately experience fire. The LG concentrations in these different biomass burning and ambient matrixes varied over nearly 4 orders of magnitude. With this, we feel the potential for widespread use of the method is fairly well illustrated, especially when considering that the heart-cutting method is now commercially-available from a major supplier. Our focus on the anhydro-sugars is justified. The importance of quantitatively measuring anhydro-sugars in the atmosphere should not be understated. These compounds are critical for apportioning biomass burning in regional air sheds. Source apportionment is a global activity that is needed to help establish regulatory compliance and understand human exposures, etc. The high quantity of samples produced over short temporal scales requires faster analytical methods for the anhydro-sugars. All samples were analyzed at N $\geq$ 3, which is well accepted in many analytical forums.

Detailed comments: Robustness? It's unclear in the presented tables and figures which samples were used and how many were used in each. Table 1 has the note n=5 and we assume these are the spiked standards. Table 2 it appears there are 4 sample types with triplicate analysis (both TE and SE). Are additional data available for SE to TE comparison? Table 3 has all 8 samples with 3 replicate analyses. I suppose the main difference between the selected compounds for Table 2 and 3 is the availability of SEâĂŘGC/MS data. It seems to me that these two data tables should be combined, so that it's more clear which samples of what types of data.

Response: Each table caption clearly states the N value. For method development and validation purposes, Table 1 includes the values obtained for spiked liquid standards as stated in lines 199-201. All the data available are included in the study. Although

ACPD

10, C1297–C1303, 2010

in principle it is simple to merge Tables 2 and 3, we have opted not to because these tables are meant to present two different perspectives on the data set. Further, merging made the information that much more difficult to interpret and presented formatting challenges regarding space. Method comparison is the major purpose of Table 2, and a complete anhydrosugar characterization is the focus of Table 3.

Why is the error for the loblolly pine so much higher than the other 3 sample types? Is there an interfering compound?

Response: We can only speculate on why the error for loblolly pine is greater. We have no knowledge of an interfering matrix compound per se. However, silyated LG at high concentrations can cause interference at m/z 206, which is a base peak target assigned to the silyated 13C-LG internal standard. Checks with standards indicated that this was a nearly negligible issue for our instrument within our calibration range at the time the loblolly pine analysis was conducted. Perhaps the biomass burning matrix was inadequately modeled by checking only standards. We also note that the solvent extraction-GC-MS analysis of the loblolly pine and CNF fire emissions, which show higher error, did occur in a different analytical laboratory than the wheat and the rice straw burns. The TE error is lower due to the automated nature of the procedure, and for TE, MS peak integration and quantification is confirmed with both primary base peak and secondary qualifier ions, which removes this interference from LG. Finally, TE replicates use small filter pieces from the same filter while trials for SE include different filters collected in parallel; thus, filter sample inhomogeneities and differences in how the filters are used are other variables that can contribute to differences in error among these samples and methods. This statement has been added to the manuscript.

In Figure 1, the authors present calibration curves for the three anhydrosugars and report 2 significant figures, however in the text the linear range is reported with 3 significant figures and the calibration is reported to be consistent over 3 orders of magnitude. This statement does not seem consistent with Figure 1.

ACPD

10, C1297–C1303, 2010

Response: Two significant figures are now reported in the text at line 216 consistent with the figure. The text was also revised to 2 orders of magnitude from 3 orders of magnitude.

I understand that an instrument schematic was previously published; it would be really nice to see this figure in this paper as well.

Response: An instrument schematic was added to the manuscript as a supplemental file. This is now mentioned in the text.

Several years ago, method development for TE was being done by another group. In their approach, they used a silylation step. Have the authors tried this approach? Is data available from the previous work for comparison?

Response: There are several research groups that have looked into the possibility of in-situ derivatization using TE. The approaches differ in many regards. One of the authors (Hays) has examined the use of tetramethyl ammonium hydroxide as a methylating reagent, but the author group has not looked closely into TE-based silyation. Our understanding is that in-situ silyation using TE is not straightforward and requires use of additional reagents to bring the working range nearer to what is acceptable for practical method use. So, despite a flurry of activity in this area and the potential importance of a breakthrough, there is still relatively limited published information about in-situ silyation using TE. With that said, we note that the main objective of the present study was to develop a fast separation method that quantitatively accounted for LG without using a derivatization step.

One of the very attractive features of SEâĂŘGC/MS methods is that they are widely applicable. The method is fairly easy and uses standard instrumentation, an obvious advantage. In this paper, TEâĂŘGC/MS is presented and is apparently very fast without the need to derivatize the polar functional groups. Can this method be applied more widely? Is the instrumentation standard? How many people have the capability to conduct 2âĂŘd separations? Can the instrument be operated remotely?

ACPD

10, C1297–C1303, 2010

Response: As discussed above, the equipment needed to perform the experiments reported in the current study are now commercially available from vendors with exposure world-wide. Although our experiments were not performed remotely, it was an option offered. A big advantage of the 2-D method presented is that standard 1-D GC-MS calibration, peak identification and quantification software are used. Thus, a scientist with 1-D GC-MS experience can potentially operate the system being described. These facts are discussed in Ma and Hays, 2008.

What are the authors implying with their comment about levoglucosan stability for almost 10 years in an ultralow freezer? Have the authors investigated storage of levoglucosan at lower temperatures for the same time periods? Are the samples collected and especially those stored over time ambient samples? We might expect ambient samples to have microbial activity and thus, the ultralow temperatures are necessary.

Response: PM filter storage at ultra-low temperatures is standard operating procedure in many aerosol characterization laboratories. Our analysis showed that LG in filter-collected biomass burning aerosols (see line 266) is stable when stored at ultra-low temperatures for nearly a decade. The effects due to storage at lower temperatures or on ambient aerosols were not examined or discussed. Depending on how the samples are handled microbial activity is a possibility for both combustion and ambient samples; however, volatility loss is potentially an even larger issue for these samples. The influence of storage time and temperature was not a major objective of the study, it was simply an unexpected opportunity that came from re-examination of archived samples – following a long period in cold storage – using a comparable method.

Related to the previous statement, does the Frasier and Lakshmanan, 2000 paper still have validity? If storage at ultralow temperature are required for levoglucosan stability, doesn't this imply that the ambient levoglucosan is not really stable?

Response: Our data imply nothing other than the LG in biomass burning PM collected on filters is stable for almost 10 years at -50 °C.

ACPD

10, C1297–C1303, 2010

On page 157, the thesis statement for the paper states that the focus of this paper is to present accurate and reproducible quantification of levoglucosan. . .with proficiency testing and comparison to silylation methods.

Response: The paper now mentions that: “Application of this method to aerosols is verified through proficiency testing and by comparing results for samples also analyzed by SE-GC-MS following silyation.”

On page 165, the range of observed levoglucosan concentrations in ambient samples is given. In figure 4 it is suggested that since the measured values are within the range, which is quite wide 0.004 to 7.6 ug/m3, then the values presented here without consideration to season or location are acceptable.

Response: The 24 hr atmospheric aerosol samples examined were from two distinct geographical regions. The time of year at which these samples were collected is provided in the experimental section. Evidence suggests that the fire activity was suppressed during collection of the KSV samples explaining the low LG value. For the KNY samples, the season factor is relatively moot considering the intensity of year-round open burning activity that occurs in urban Kenya. Regardless, the values presented for these regions are well within values reported world-wide in the literature. Again, the focus here was to demonstrate analytical capability, not necessarily to examine the seasonal or geographical distribution of LG.

In this reviewer’s opinion, a more direct sample comparison is need to compare TEâĂŘGC/MS to SEâĂŘGC/MS or HPLCâĂŘPAD. While I agree that the four samples presented are promising in this regard, it appears to be contradictory to the title statement that this method is fast and easy because the analysis is of underivatized levoglucosan.

Response: There are actually eight different aerosol samples being examined as part of the current study, and the aerosol matter itself should have quite minor, if any, influence on the speed of the analysis. Moreover, neither the title nor the manuscript

ACPD

10, C1297–C1303, 2010

claims the whole method is simple or “easy” as the reviewer suggests. The analytical community generally agrees that the sample preparation associated with TE is simpler and offers potentially higher throughput, and we state so. We understand that performing SE on samples in batch can help make up for some of this difference and we now mention that in 3.3.1 Overall method analysis times. We clearly state that from start-to-finish our analysis time is 32 min, whereas for the SE methods the silyation reaction alone takes at least one hour to complete. We understand PAD is faster. However, preparation times prior to injection can be somewhat lengthy. These points are given as well.

Perhaps more a question of style, but in my mind still worth mentioning, is that there are very many acronyms used in this paper. Quite a few of these acronyms are not used more than a few times, making their occasional use quite distracting. Along these lines, since the paper is about three anhydrosugars, why not just use their names throughout the manuscript.

Response: The word levoglucosan is used more than fifty times in the manuscript. Combined the words mannosan and galactosan are used more than twenty times. Therefore, it seems acceptable to use acronyms that have been used before in the open literature to refer to the compounds names.

Minor comments: On page 159, what is MSP? Is this a manufacturer or sampling site location? Response: MSP is a manufacturer, stated in line 132.

What is PMT? Response: PMT stands for PM sample collected in piedmont region, NC, which is stated in line 138-140, also in the caption of Table 3.

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