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Discussions

Interactive comment on "Determination of n-alkanes, PAHs and hopanes in atmospheric aerosol: evaluation and comparison of thermal desorption GC-MS and solvent extraction GC-MS approaches" *by* Meng Wang et al.

Anonymous Referee #4

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Reviewer comments on amt-2019-4

The authors present a comparison between between analysis of organic particle components using solvent extraction versus thermal desorption. In general, I think it is important to do careful methodological analyses, as is the goal of this work. The overall upshot conclusion is that TD is as good a method as SE, which is a valuable conclusion. However, if the focus is on details of the comparison, there are several major shortcomings of the manuscript as it is currently presented. These are described in general comments below. If the focus is on the scientific comparison between the

cities, substantial additional conclusions and discussion would be warranted, as well as better justification for some of the current conclusions of the work (i.e. n-alkanes are not a very compelling way to distinguish biogenic an anthropogenic emissions). My overall impression of this work is that it provides good supporting information that their extraction techniques work, but falls short of providing either a comprehensive analysis of their techniques, or a compelling scientific analysis of their data. With this in mind, it is more suited for the supplementary material of a separate manuscript that does the latter.

General comments:

Gaps in methodological details: The efficiency and quality of thermal desorption is expected to be strongly dependent on the flow rates and paths of the desorbed analytes. If this is a commercially available system (e.g. Gerstel TDU, or Markes TD-100), the authors should provide that information and do not need to describe flow paths in detail. If it is custom built, some detailed description is necessary.

Was there cryogenic trapping of the desorbed analytes for focusing? Many TD systems (e.g. Gerstel and Markes) desorb at high flows to a low-volume cryo trap, backflush that trap. No mention of that approach is made here. Later data (e.g. Figure 1) indicates possible loss of higher-volatility analytes, which might be improved with a cryo trap. If one is not used in this case, I question the application of this intercomparison to many currently available TD systems.

What volume of solvent extract was actually injected? (I assume ~1 uL)

Concerns in intercomparisons: How is "recovery" calculated? Recovery of C36 for SE is 100%, yet its peak is much lower. Given that response of an MS is non-universal and not directly related to mass from first principles, what is the SE C36 signal being compared to in order to determine it is 100%? Or is the decrease in peak height just due to peak broadening and the integrated area is the same for all alkanes? If that is the case, my suggestion for re-doing Figure 1 would make it much more clear.

Regarding LODs, the comparison between TD and SE is self-evident. TD analysis sends all introduced sample to the GC/MS, while SE dilutes sample to ~1 mL, of which <1 uL (I'm assuming based on typical methods, it is never actually stated) is injected to the GC/MS. For the same amount of sample, TD should be ~1000x more sensitive, which is what the authors find on Page 6.

Issues with scientific conclusions:

Particle emissions from vehicles also contain n-alkanes larger than C26, so it is not necessarily true those are indicative of biogenics. In fact, looking at Figure 4, all 4 cities exhibit n-alkane patterns centered around C24-C26, as would be expected for organic particles emitted from motor vehicles. Evidence for biogenic influence may be present based on odd-even ratios at Shanghai, but in general drying any anthro vs bio conclusions from the n-alkanes is questionable. Differences in n-alkane distributions may be due to differences in fuels or emissions. (Why not use pinic acid, or small acids, or other analytes, as evidence of biogenic influence?) (Worton, D. R.; Isaacman, G.; Gentner, D. R.; Dallmann, T. R.; Chan, A. W. H.; Ruehl, C.; Kirchstetter, T. W.; Wilson, K. R.; Harley, R. A.; Goldstein, A. H. Lubricating oil dominates primary organic aerosol emissions from motor vehicles. Environ. Sci. Technol. 2014, 48 (7), 3698–3706.)

A lot of discussion in the paper is of specific differences in concentrations between the cities, but there is not much context or discussion of the importance or reasons for these differences. When reasons are discussed, they are broad claims based on little data (such as the anthro v. bio discussion commented on above, or the general comments around residential fuel use in Beijing)

Technical comments:

Page 2 line 5 - Wording is a little odd. What exactly is "much less constrained"? The composition?

Page 2 lines 9-10 - The fraction of particulate matter identified depends strongly on

composition and sources. This is probably a reasonable statement in general, but it is a little narrow, non-specific, and perhaps a bit out of date. As examples of cases where this statement might not be true: - in the Amazon nearly 30% is just from 2-methyltetrols and C5-alkene triols, which are identified as specific compounds (see Hu, W. W.; Campuzano-Jost, P.; Palm, B. B.; Day, D. A.; Ortega, A. M.; Hayes, P. L.; Krechmer, J. E.; Chen, Q.; Kuwata, M.; Liu, Y. J.; et al. Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements. Atmos. Chem. Phys. 2015, 15 (20), 11807–11833.) - in the central valley of California most of the signal is a complex mixture of hydrocarbons that have been characterized in detail (see Chan, A. W. H.; Isaacman, G.; Wilson, K. R.; Worton, D. R.; Ruehl, C. R.; Nah, T.; Gentner, D. R.; Dallmann, T. R.; Kirchstetter, T. W.; Harley, R. A.; et al. Detailed chemical characterization of unresolved complex mixtures in atmospheric organics: Insights into emission sources, atmospheric processing, and secondary organic aerosol formation. J. Geophys. Res. Atmos. 2013, 118 (12), 6783–6796.) - In the southeastern US, ~50% of signal can be accounted for by individual molecules that are oxidation products of individual precursors, and anoth ~25% characterized by molecular formula. While this falls short of being "identified as specific compounds", it is much closer to complete characterization than implied by this sentence (see Zhang, H.; Yee, L. D.; Lee, B. H.; Curtis, M. P.; Worton, D. R.; Isaacman-VanWertz, G.; Offenberg, J. H.; Lewandowski, M.; Kleindienst, T. E.; Beaver, M. R.; et al. Monoterpenes are the largest source of summertime organic aerosol in the southeastern United States. Proc. Natl. Acad. Sci. 2018, 115 (9), 2038–2043.) I recommend tring to be a little more specific or add caveats to this claim (e.g. "In many environments..." or "using traditional techniques")

Page 2 lines 21-22 - many of the citations you reference above actually are comparisons between SE and TD. How does this work specifically advance the knowledge?

Page 4 line 25 - What volume of these standards?

Figure 1 - The chromatograms are interesting, but it would be much easier to intercom-

pare if they were all on the same plots and axes. Why not overlay lines representing the integrated peak area in each case, something more like Figure 2a? Then we could intercompare and better understand differences.