Review of Orasche et al.

General comments:

Orasche et al. present a novel thermal extraction/in-situ derivatization technique for simultaneous GC-MS measurement of polar and non-polar organic entities in the aerosol matrix. The work is a nice advancement since separate polar and non-polar GC-MS measurements of aerosols is relatively tedious. Sheesley et al. 2010 [1] provide a nice example of the power of thermal extraction-GC-MS coupled to in-situ derivatization and their study should be referenced here. The review of Hays and Lavrich [2] also supports the need for such methods. Perhaps it isn't as important to those interested in the atmospheric chemistry of aerosols, although there is a significant body of science produced using related in-situ reaction techniques (e.g., solid-phase microextraction). It may be worth exploring and calling attention to some of this literature as well.

The ACP readership will be interested in the topic of this study; however, it may be too exhaustive for a "technical note". I think the readership would benefit more from a shorter version of this submission that covers the salient points of the analysis and describes how the method is best implemented. Understand that there have been several comparisons between TE and SE as of late, especially for PAH (see [3-5]). And while such comparisons are important, it may be possible in this case to briefly mention that what other groups have already observed was also confirmed for the present study. This can be done without delving into too much further detail. So, Figures 4 and 5a and b can be reduced to include only a few representative compounds or placed in supporting information, Tables 1 and 2 are also good candidates for Supporting Information.

The submission would benefit from the addition of a chemical figure depicting the reaction scheme being studied.

Specific comments:

The abstract should contain quantitative information. Consider adding information about LOD/LOQ, calibration, dynamic range etc.

p.15256, lines 20-25: it may be worth explaining the difference between the thermal "extraction" and "desorption" terms. Thermal extraction is using heat to remove something from its native matrix. Desorption implies the removal of trapped analyte from Tenax or similar carbon sorbent.

p.15256, lines 20-25: Are analyte loss and memory effect reductions really advantages of DTD? I mean the temperature of the GC injector is no different than thermal extraction temperatures or the temperatures solvent extracts are subject to. How does DTD improve discrimination? Please be clear.

p.15257, lines 1-5: Shorten the sentence beginning "Since a growing…" by breaking it into two sentences.

p.15257, lines 15-20: This may be a good point to introduce the work accomplished by Sheesley et al. 2010.

p.15257, lines 20-25: Provide an example of how polars play a role in the atmosphere.

p.15257, lines 25-30: "colophony"? Not sure about this word. Probably should be replaced.

p.15258, line 6: Please define the term "reaction velocities". Not sure what this is.

p.15258, lines 8-13: This is certainly an interesting discussion, but I'm curious: Why not just swap out the column for something more amenable to polar compound analysis? For example, use a wax column instead. Do we really need to go through reagent addition to convert these compounds? Why not use HPLC for these compounds? HPLC is capable of PAH analysis and is highly sensitive to many polar compounds as well. Shouldn't these methods be included as part of this discussion? I think it's important to compare these methods and clarify why DTD is a method of choice.

p.15259, lines 2-3: "Delicate" is not the correct word to describe PAH because they are relatively stable under the conditions being used here. o-PAH, ok…maybe….but not the PAH.

p.15259, lines 24-25: Are the authors certain that this reaction is heterogeneous, that is, occurs between the gas (reagent) and solid (aerosol particle) phases? Where is the evidence for this? Please explain.

p.15260, lines 6-13: Why are both reaction routes necessary? Why soak the sample with reagent and deliver the reagent in the gas-phase? Please explain in the paper.

p.15261, lines 10-11: It may be interesting to note that ^{13}C-levoglucosan is best used with high-resolution MS. Low-resolution MS shows a contribution for two ions at the base peak commonly used for quantification.

p.15261, line 17: Why was sodium sulfate added? Briefly explain.

Sections 2.5 and 2.6: These sections aren't quite clear. When was the reagent delivery in the carrier gas on/off? What was the standard addition matrix and why was standard addition used to calibrate? Standard addition is not typically applied for calibration. It is used to understand matrix effects contributing to analyte quantification. The term may be being mis-used here.

p.15264, lines 1-5: Please revise the sentence "The first fraction eluted…." for clarity.

p.15265, lines 25-26: There really isn't any evidence presented here that DTD increases reaction speed and yields. Is there?

p.15266, lines 2-3: Not sure what eicosane-d_{42} has to do with anything being discussed here. It should not be influenced by the reaction.

p.15266, lines 12-19: Little or no evidence is presented for several of these itemized advantages. At the very least, the authors should point out that this is speculation or offer some literature evidence for these advantages.

p.15266, line 29: Report the error associated with this finding. In other words, how many times was this experiment tried? Was it reproducible?

p.15267, lines 1-2: In what context. How are B[a]P and pyrene reactive?

p.15267, lines 13-15: Why call this an SE cal method when standards dissolved in solvent were directly injected? The extraction process has nothing to do with this?

p.15268, line 18: How relevant are the LOD values being reported. These seem to ignore the fact that DTD requires less PM sample for analysis. Wouldn't this technically make the method more sensitive? Yet it doesn't appear to be that way in this study.

p.15269, lines 1-3: Figure 3 suggests there is an effect. Can we be more specific? Also, what types of artefacts are being referred to here? Please explain in the paper.

p.15269, line 28: Explain how the substrate is "deactivated". The term affinity is better than "affection" for this case.

p.15271, lines 1-5: The description can be removed from the paper. It's inherent.

p.15271, line 26: Can these variations be quantified?

p.15272, lines 19: "sterical advantages" Not sure about what this is. Also, please be specific about what functional group is being influenced and about where it is located on the molecule.

1. Sheesley, R.J., et al., *Temporal Trends in Motor Vehicle and Secondary Organic Tracers Using in Situ Methylation Thermal Desorption GCMS.* Environmental Science & Technology, 2010. **44**(24): p. 9398-9404.

2. Hays, M.D. and R.J. Lavrich, *Developments in direct thermal extraction gas chromatography-mass spectrometry of fine aerosols.* TrAC Trends in Analytical Chemistry, 2007. **26**(2): p. 88-102.

3. Ho, S.S.H. and J. Yu, *In-injection port thermal desorption and subsequent gas chromatography-mass spectrometric analysis of polycyclic aromatic hydrocarbons and n-alkanes in atmospheric aerosol samples.* Journal of Chromatoraphy A, 2004. **1059**(1-2): p. 121-129.

4. Ho, S.S.H., et al., *Evaluation of an in-injection port thermal desorption-gas chromatography/mass spectrometry method for analysis of non-polar organic compounds in ambient aerosol samples.* Journal of Chromatography A, 2008. **1200**(2): p. 217-227.

5. Lavrich, R.J. and M.D. Hays, *Validation Studies of Thermal Extraction-GC/MS Applied to Source Emissions Aerosols. 1. Semivolatile Analyte-Nonvolatile Matrix Interactions.* Anal. Chem., 2007. **79**(10): p. 3635-3645.