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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Technical Note: In-situ derivatization thermal desorption GC-TOFMS for direct analysis of particle-bound non-polar and polar organic species" *by* J. Orasche et al.

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Thanks a lot for the well-founded comments. In the following we will discuss these comments:

First of all the references which are recommended will be added in a revised version. We also agree to transfer some of the figures and tables to supporting information and to add a depicting figure of the reaction.

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

Although it is a technical note we do not agree that it is necessary that quantitative information is found in the abstract. Nevertheless we will provide an example e.g. for levoglucosan.

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.

We think both terms have a piece of truth. The term extraction implies the use of a solvent for removing analytes from their matrix whereas desorption implies the use of a kind of energy, in our case heat, to remove analytes. The other reason for using "thermal desorption" was that it is established in our group since some years [1, 2]. We demonstrate here that IDTD is a front-end of DTD.

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.

DTD is a near on-column technique. The desorption inside of the injector with the

shortest way to separation column as possible (no cold spots) and the use of a fresh glass liner for every sample are two important properties of this technique. These two options eliminate the possibility of memory effects and analyte loss by working without a transfer line.

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

Yes, we will do this.

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

Yes, that's right. We will consider this for the revised paper.

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

We will add some sentence like this: "Although a lot of polar compounds have direct sources (mainly biogenic sources) an important pathway of generation is the formation of secondary organic aerosols. The rising amount of polar species up to water soluble organic compounds (WSOC) during aerosol ageing leads to an increase of hydrophilic properties of particles and a growth of probability to condense water on particle surface. These hydrophilic particles are so called Cloud Condensation Nuclei (CCN)."

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

Colophony is a synonym for rosin. It origins from the name of the ancient greek city Colophon a former trading center for rosin.

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

This has to be replaced by "reaction rate".

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.

Like DTD IDTD is a less time consumption method with relatively low costs compared to solvent extracting methods followed either by HPLC or GC. Moreover the possibility of in-situ-derivatization is something like a front-end for existing DTD systems. Of course for HPLC it is not necessary to derivatize components. But with IDTD it is not necessary to pre-treat samples in any extensive way. A very interesting technique without derivatization procedure is a fast two-dimensional gas chromatography method that uses heart-cutting and thermal extraction (TE-GC-GC-MS). Yet it seems to be established for anhydrous sugars, n-alkanoic acids, substituted phenols, and nitrogen-bearing heterocyclics [3, 4]. The combination of a non-polar separation phase with a polar one provides quantifiable sharp peaks in the chromatograms. Compared to GC systems with highly polar separation columns IDTD is a more sensitive way to transfer delicate molecules from injector to column.

We will add this passage in the revised paper.

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.

We will try to answer this further down.

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.

No, we do not suggest that the reaction is heterogeneous. We only reveal that "derivatization and desorption of polar organic compounds occurs directly from particulate matter on the filters" – clarifying that no further preparation steps are necessary and that it is really an in-situ technique.

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.

This is an interesting aspect which should be discussed more in detail than in the existing manuscript. Therefore we will add some words about it in the discussion part "3.1 Derivatization" starting at page 15265. It is also associated with your question before where the reaction occurs. We observed that for silylation of multifunctional molecules like levoglucosan or polycyclic molecules like resin acids or sterols the soak of the sample is necessary. On the other side smaller molecules like most phenols or small acids can be derivatized only by addition of MSTFA during the desorption process. So reactions take place in multiple ways. By the way, please read also our statements to the comments of referee 2.

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

Well, this fact concerns the pair of base peaks 204/206 (m/z native / m/z 13C6-levoglucosan). As shown in the table 1 we are using the peaks 217/220 for quantification. We are also using the minor fragment peaks at m/z 333/338 for checking the quantification of levoglucosan. In most cases the abundance of this pair of peaks

is high enough for quantification due to the high concentrations of levoglucosan in the atmosphere. Then even low resolution MS have no problems.

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

Like described in line 16/17 it is necessary for dilution of the Standard Reference Material (SRM). Otherwise it would not possible to weigh out the small amounts of SRM which are required for thermal extraction. The used sodium sulphate was free of water and is an inert matrix.

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.

The standard addition method is used here to minimize the matrix effects (see section 3.2 in the discussion). We use PM samples like described in section 2.5 as reference samples. These samples are from our aerosol characterization site in Augsburg, Germany where most of our samples were collected.

The delivery of MSTFA was switched on after temperature reached 300 °C and was closed before the injector was cooled down. We will define this more precisely in section 2.4. The usual DTD method like described in section 2.6 can still be used. In that case the valves stay closed and no MSTFA is added.

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

These two sentences will be replaced by: "First alkanes were eluted from the column by a solvent mixture of hexane/dichloromethane (9:1, v/v). In the second and third fraction

PAH and o-PAH were eluted after each other by hexane/dichloromethane (1:1, v/v) and dichloromethane/methanol (19:1, v/v) respectively (all solvents: Merck, Germany)".

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

Maybe the term yield is here ambiguous. What we want to say is that the reaction rate at 300 °C is higher than at 80 °C like used for the solvent extracted samples. In the section before (2.8) we describe that we need 3 hours derivatization time. With IDTD we need only 20 minutes to obtain the same derivatization yield.

p.15266, lines 2-3: Not sure what eicosane-d42 has to do with anything being discussed here. It should not be influenced by the reaction.

That's the reason why we use it as a recovery efficiency standard. We calculated the derivatization yields by help of this standard (minimizing any influences by sample matrix or sensitivity of the instrument). We will add this for clarity.

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.

Yes, we suggest that these facts are possible advantages of the method. Due to a similar comment by referee 2 we discuss point (1) there. Point 2 and 3 are based on the observations made due to point 1. Point 4 is a fact which is controlled by the valves opening and closing the pathway to add MSTFA into the carrier gas. Point 5 is a fact that is verifiable like described in p. 15266, lines 19-4 (following page).

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

Like mentioned at the next page, line 4, we verified this by analysing eighteen samples with DTD and also with IDTD. Since the filter precipitations were quite similar and rather low (47 mm filter diameter, 2.3 m^3 per hour low volume sampling, 1 hour sampling time with PM1 cut-point) for all of the eighteen samples we found reproducible results. Maybe we will describe this more detailed.

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

This and the term "delicate" for PAH is accounted for the possible reactions of PAH with oxidants during thermal desorption. Especially BaP and pyrene are known to react with oxidants. Although references [5-7] studied the behaviour of these compounds in the atmosphere we found that under some conditions like described in section 3.1 and shown in figure 3 degradation of BaP and pyrene is possible.

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?

No, we call it not a SE cal method. But it is right that standard solutions were not treated in any extraction procedure. Only the final reduction step with following addition of silylation reagent is involved. Therefore we work with isotope labelled standards and a recovery efficiency standard.

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.

Yes, that's right. The values are absolute values (unfortunately we found even a failure in our calculation formula). Therefore we calculate the LOD values more comparable for SE vs. IDTD per analysis/sample. We will exchange the values for the revision.

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.

In page 15269 we only refer to the calibration. This means the effect like shown in figure 3 was not affecting the quantified results. The ratio between native and isotope signal were not influenced.

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

We believe that filter matrix is deactivated. This means that polar quartz surfaces were silylated like often used for deactivating glass ware.

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

Okay.

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

For 9,10-Anthracenedione and Cyclopenta[def]phenanthren-4-one we found values more than 50 percent over those found with the solvent extraction method.

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.

Levoglucosan provides three functional hydroxyl groups which are located in alternating planes. Its isomers mannosan and galactosan have each two neighbouring hydroxyl groups which are in the same plane. These hydroxyl groups maybe steric hindered when substituted by trimethylsilyl groups. A figure will be added for the anhydrous sugars.

[1] Schnelle-Kreis, J., Welthagen, W., Sklorz, M., Zimmermann, R. (2005). Application of direct thermal desorption gas chromatography and comprehensive two-dimensional gas chromatography coupled to time of flight mass spectrometry for analysis of organic compounds in ambient aerosol particles. Journal of Separation Science, 28(14), 1648-1657.

[2] Schnelle-Kreis, J., Sklorz, M., Peters, A., Cyrys, J., Zimmermann, R. (2005). Analysis of particle-associated semi-volatile aromatic and aliphatic hydrocarbons in urban particulate matter on a daily basis. Chemosphere, 39(40), 7702-7714.

[3] Ma, Y., Hays, M. D. (2008). Thermal extraction-two-dimensional gas chromatography-mass spectrometry with heart-cutting for nitrogen heterocyclics in biomass burning aerosols. Journal of Chromatography A, 1200(2), 228-234.

[4] Ma, Y., Hays, M. D., Geron, C. D., Walker J.T., Gatari Gichuru, M.J. (2010). Technical Note: Fast two-dimensional GC-MS with thermal extraction for anhydro-sugars in fine aerosols. Atmospheric Chemistry and Physics, 10, 4331-4341.

[5] Nielsen T, Ramdahl T, Bjï£¡rseth A 1983. The fate of airborne polycyclic organic matter. Environ Health Perspect 47:103-114. doi:10.1289/ehp.8347103

[6] Miguel, 1984 A.H. Miguel, Atmospheric reactivity of particulate polycyclic aromatic hydrocarbons collected in an urban tunnel, Sci. Total Environ. 36 (1984), pp. 305–311.

[7] Liu, Y., Sklorz, M., Schnelle-Kreis, J., Orasche, J., Ferge, T., Kettrup, A., Zimmermann, R. (2006). Oxidant denuder sampling for analysis of polycyclic aromatic hydrocarbons and their oxygenated derivates in ambient aerosol: Evaluation of sampling artefact. Chemosphere, 62(11), 1889-1898.