

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.

J. Orasche et al.

juergen.orasche@helmholtz-muenchen.de

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We also would like to thank referee 2 for the well-founded comments. In the following we will discuss these comments:

Occasionally the author use terms like “...quite good...” and “...somewhat...”. (e.g. page 15268, line 16-19 and 26-27, page 15271, line 12, 16, 22-23, 26). Please be more precise. In some cases when these statements are used the manuscript would benefit if the findings would also be compared to typical values found in other studies in the literature. E.g. can the authors compare their precisions achieved for their SE, IDTD measurements compare to similar conducted studies using DTD and/or SE for this range of compounds? This would allow the reader to better assess how well the novell IDTD techique works. Also especially in section 3.4 on some occasions terms/combinations of “somewhat lower/higher correlation coefficient/variations” are used. Can these variations be quantified to provide the reader with numbers to better evaluate the comparison of the methods?

page 15268,

line 16-19: Other studies using GC-MS methods obtained precisions of 20% [1, 2], 5% [3] and 2-5% [4]

line 26-27: “Anyhow, correlation of quantitative results from IDTD with the solvent extraction method is quite good with a slope of the correlation regression near one”

Section 3.4 and especially page 15271, line 12, 16, 22-23, 26: We will work out some comparisons with other studies to clarify some subjective terms.

page 15256, line 1-3. In the first sentence the author state that the IDTD-GC-TOFMS was developed for determination of polar organic compounds. However the title of the manuscript suggests a study of “non-polar and polar organic species”. This is confusing. Please revise.

Yes, we will revise it for clarity.

page 15256, line 9 (see also page 15260, line 12-13 and page 15265, line 25-26). Does the derivatization speed/rate really increase by heating to 300C? If possible measurements should be provided to back up the authors statement.

Reaction rate for IDTD is higher than for SE at 80 °C. This statement we made due to the comparison of derivatization yields (section 2.8). With IDTD we need only 20 minutes to obtain the same derivatization yield as for the SE method where we need 3 hours of reaction time.

page 15257, line 12-13 What does the authors mean with "particle fractions"? To my knowledge the TAG instrument samples and collects aerosol samples (using a PM2.5 cyclone) not fractions of it. Please explain.

The TAG system collects particles with a cut-point of PM2 by impact in a thermal desorption cell. Due to alternating sampling/analysis and thermal desorption no online analysis of gaseous phase of aerosols seems to be possible.

page 15258, line 9-13 The author should discuss briefly why they think it is "essential" to have in general derivatization steps. Common techniques exists (e.g. GC and 2d-GC using columns with a highly polar mobile phase, HP-LC etc.) which can detected reliably and quantifiable many polar compounds. The pros and cons of these techniques compared to derivatization should briefly be mentioned. What are the benefits of IDTD compared to these methods?

Due to a similar comment of referee 1 we discussed it already there.

page 15260, line 7-9. Could the author explain briefly how the moisturizing of the filter is done? Is also the saturated carrier gas used to stream over the filter using a low-injector temperature or is this a separated automated introduction of MSTFA through

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different means? This is also interesting to know in conjunction with my comment below (page 15266, line 8-11).

To soak the filter with MSTFA we use the automatic sampler which adds 10 µl directly onto the filter by syringe injection prior to installation of the glass liner with the sample into the injector (also done by the automatic sampler). We will specify this information in the paper.

page 152663, line 1-11. The last paragraph of section 2.4 and section 2.5 are almost identical. Please revise these two paragraphs.

Yes, we will do this.

page 15266, line 8-11. This might be an interesting question to discuss. Did the author tested if polar compounds degrade before they are derivatized using only the MSTFA saturated carrier gas stream to flush it over the sample while heating the injector? It would be very interesting to know if high derivatization yields could be achieved using only a saturated carrier gas stream starting with a cold injector for some time and then subsequently heat it up.

Yes, it is an interesting aspect which allows us to tell something about the history of the method. We started experiments first by adding BSTFA/TMCS (v/v 99/1) on filter samples. Due to problems with TMCS by generating of HCl and the higher boiling temperature of BSTFA we tried to work with MSTFA. Since MSTFA has a low boiling point it has two crucial advantages. First we have nearly no problems with MSTFA during detection due to short retention times in gas chromatography. The second important point is the high vapour pressure at room temperature. No additional heating is necessary to get enough vapour into the carrier gas stream. Our first steps with MSTFA (only wetting filter with MSTFA) were ambivalent. We got good results especially for anhydrous sugars. But it was not possible to reach good results for some phenols (especially sinapinic acid), resin acids and aliphatic acids. And therefore it was impressing

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as we tried the first time the enrichment of carrier gas with MSTFA. We had immediate success (we got signals for two of our standard substances sinapinic acid and isopimaric acid, we had not detected before). But on the other side without damping the filter, substances like levoglucosan are not or only partially derivatized. So, up to the question: We haven't tested the degradation of compounds. Reliable results maybe only possible testing single substances when using a direct inlet to the MS. Degradation like seen for the PAH were not directly indicated. We will consider this in the paper and additionally point out the fact that incomplete derivatization is also possible.

page 15266, line 12-14. This manuscript doesn't seem to provide data which actually shows that the MSTFA saturated carrier gas flow protects the derivatized compounds. This statement should be supported by data.

The statement is based on two observations. First of all it is based on the described effect of protection of PAH by MSTFA in the carrier gas. And the second thing is a high water content of samples collected on quartz fibre filters. This is indicated by a large signal at m/z 147 caused by Hexamethyldisiloxane (base peak at m/z 147) during thermal desorption. This signal is caused only to a minor content by MSTFA itself (base peak m/z 77 next to unspecific 73)! These facts can only be observed when working without desorption delay time which is used usually to prolonging lifetime of the MS filament (similar to solvent delay).

Without a surplus of MSTFA the water content could be responsible for a competitive reaction next to derivatization of analytes and water can also react with already derivatized analytes during derivatization / desorption process. We will discuss this in more detail in the revised paper.

page 15271, line 1-5. The explanation of a correlation plot is not necessary. The part should be deleted.

Yes, it will be deleted.

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page 15271, line 15-17. The author state "Retene exhibited a good comparability but a somewhat lower correlation coefficient. Experiences indicate higher variations of retene when analysed by thermal desorption methods." Please provide a reference to back up this statement.

We mean the experience of our group with TD since many years. Nevertheless we will delete this sentence due to the fact that variations of retene are much smaller with IDTD than with our original DTD method.

page 15271, line 12. I assume it should read "IDTD" instead "DTD"

Yes, that's right.

page 15272, line 14-17. It would be instructive to briefly add information how LOD (e.g. S/N greater than 5) and LOQ (e.g. 10xLOD) was derived.

Yes, and like we already replied the first referee we will revise the table to provide LOQ values which are more comparable for SE vs. IDTD comparison. We will calculate LOD per analysis/sample. In advance we can give a first description how LOQ's were calculated:

"The limit of quantification (LOQ) of the method is defined as the minimum amount of substance that is according to the minimum reliable signal plus nine times (three times for LOD) the standard deviation of this underground signal."

page 15272, line 17-21. I'm wondering why the correlation for mannosan (0.826) is as bad as galactosan (0.83) with mannosan having 10 times more signal. The authors state this is due sterical hindrance resulting in lower derivatization yields for galactosan and mannosan. However I would have assumed that with a signal ten times higher the effect would have been less for mannosan resulting in a better correlation coefficient.

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It would be good if the authors could provide additional discussion to explain their statement further.

As described in section 3.2 and in the conclusions we recommend the use of a large number of isotope labelled standards. The reaction rate and yield of the three anhydrous sugars could be rather different due to their stereo isomeric differences. The concentrations of these sugars in the ambient air samples were all in the linear range of their calibration curve using ¹³C6- levoglucosan as internal standard. Therefore no differences in correlation of comparison of IDTD/SE were observed.

Figure 1, injector blow-up. The text describing the different parts of the injector should be larger. Please also indicate where the MSTFA inlet is.

Yes, we will revise it.

Figure 2. All peak annotations, axis descriptions and values are almost not readable. Please revise.

Unfortunately the discussion paper is optimized for screen version. Even the printer friendly version includes two page of the manuscript on one print page. Although the figure is a vector graphic and therefore zoom-able we will provide a more printer friendly version.

Figure 5a,b,c: Please say something about errors of the measurement shown and add error bars to the graph or give an error bar cross in a corner of each graph. This allows the reader to better assess how well the data points scatter around the line through the origin.

Yes, we will add the error bars.

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[1] Graham B, Guyon P, Taylor PE, Artaxo P, Maenhaut W, Glovsky MM, Flagan RC, Andreae MO (2003) J Geophys Res Atmos 108(D24):AAC 6–1, 6–13

[2] Graham B, Mayol-Bracero OL, Guyon P, Roberts GC, Decesari S, Facchini MC, Artaxo Maenhaut W, Koll P, Andreae MO (2002) J Geophys Res 107(D20):8047

[3] Simpson CD, Dills RL, Katz BS, Kalman DA (2004) J Air Waste Manage Assoc 54:689–694

[4] Pashynska V, Vermeylen R, Vas G, Maenhaut W, Claeys M (2002) J Mass Spectrom 37:1249–1257

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