

## ***Interactive comment on “Development of parallel sampling and analysis for the elucidation of gas/particle partitioning of oxygenated semi-volatile organics: a limonene ozonolysis study” by S. Rossignol et al.***

**S. Rossignol et al.**

[laura.chiappini@ineris.fr](mailto:laura.chiappini@ineris.fr)

Received and published: 3 May 2012

The authors wish to thank both reviewers for their conscientious reading of the manuscript and their constructive comments. The text was modified and clarified and a response to each comment is provided below.

Response to Referee #1

Major comments:

- (1) "The authors should thoroughly revise the manuscript with respect to the English C865

usage as there are a lot of spelling and grammatical mistakes, and unsuitable words are used (see the separate document with suggestions for improvement). Even in the title it seems that a word is missing (Development of a parallel sampling and analysis method for the elucidation of gas/particle partitioning of oxygenated semi-volatile organics: A limonene ozonolysis study). Furthermore, nearly all chemical names in the tables are incorrect and should be properly corrected (hyphens, lower-case letters, and italics)."

Answer to Reviewer: The authors want to greatly thank the reviewer for English revision of the whole submitted manuscript. All corrections were taken into account. Chemical names, in the text, in the tables and in the figures, were also properly corrected.

(2) "The determination of partitioning coefficients must be better explained. From a first reading it seems that gas and particle phase concentrations were determined from the parallel sampling set-up using TENAX cartridges and filters. This approach is not sufficient as both techniques suffer from high uncertainties. I wonder why different types of filters were used (quartz filters for derivatisation with PFBHA and Teflon-quartz filters for derivatisation with MTBSTFA). Especially for the carbonyl compound analysis a very high positive artefact is expected using quartz filters. In addition, no pre-treatment for the quartz filters is described that might give a hint for high blank values. I suggest a comprehensive discussion of possible problems to determine  $K_i$  values and that the determined  $K_i$  values in this study represent the best estimates under the conditions applied."

Answer to Reviewer: Precisions on filter choices were added in Sect. 2.1.4 ("Filters"). Teflon-quartz filters were chosen for derivatisation with MTBSTFA mainly as they reduce both moisture loading and hydroxyl/carboxyl compounds interactions with filter media. Nevertheless, quartz filters were used for derivatisation with PFBHA as this derivatisation reaction requires moisture for its achievement and as this type of filter is the best compromise between moisture loading and thermal resistance. Pre-treatment protocols were given in the same Sect. 2.1.4 (page 1164 line 21: "Before use, quartz fibre filters were conditioned by heating at 450°C for 5 hours and Teflon-quartz filters

by heating at 300°C for 5 hours"). We are aware that quartz filters can induce positive artifact by gas adsorption. However, the developed method allows the use of denuder in order to trap gas compounds upstream the filter, even if that was not the case in the present study. For the presented ozonolysis experiment, details on experimental partitioning coefficients calculation were added in Sect 4.2.3, including the precision that "partitioning coefficients represent the best estimates under the conditions applied". As mentioned by the reviewer, besides eventual artefacts, the developed method suffers from uncertainties on gas- and particulate-phase compound quantification. However, this is shared by all quantification techniques, and the developed method seems to be a real improvement compared to existing methods for partitioning coefficient determination, as it is fast, sensitive and solvent free. Furthermore, uncertainties on experimental partitioning coefficient calculation were corrected in the revised manuscript as an error was done. Explanations are given in the supplement to this final author response.

(3) "All figures show the determined peak area for each compound. This is not a suitable analytical approach to evaluate a method. Especially, when authentic standards are available and satisfactory calibration curves are obtained (as shown in Table 1) each sample could be quantified using the obtained calibration curves. Changes in detector response and other method uncertainties are not taken into account when only the peak area is used."

Answer to Reviewer: This work was performed in two successive phases. The first one concerned the characterisation of the parameters influencing the derivatisation efficiencies and the compound recoveries (humidity influence, breakthrough volumes, derivatisation efficiencies compared to in-solution derivatisation) in order to choose the better way to construct relevant calibration curves for sample quantification. As a result, calibration curves were only constructed once, in the second part of this development work, after parameters optimisation. Most of the characterisation tests were performed only on the TD-GC-FID system owing to the FID response stability over time (tested by the injection of a benzene standard solution each week) allowing direct comparison

C867

of obtained results, even in the case of only the determined area peak was taken into account. For the method characterisation tests, the calibration curves construction and the samples analysis performed on the TD-GC/MS system (in EI mode), the changes in detector response were daily checked by injecting either a standard solution of octane, benzaldehyde and 4-heptanone (in-solution derivatised with PFBHA) or a standard solution of octane, phenol, valeric acid and perillic acid (in-solution derivatisation with MTBSTFA). Reproducibility of in-solution derivatisation was previously tested.

Specific comments:

1) "Abbreviations: need to be defined the first time that they are used in the main text and only need to be defined once."

Answer to Reviewer: Abbreviations were defined, only the first time that they are used.

2) "Terms relating to mass spectrometry: I suggest that the IUPAC guidelines be followed. These guidelines can be found in the following publication: "Standard definitions of terms relating to mass spectrometry (IUPAC Recommendations 2006)" by Murray et al. ([http://old.iupac.org/reports/provisional/abstract06/murray\\_prs.pdf](http://old.iupac.org/reports/provisional/abstract06/murray_prs.pdf)). Example: the term "Electron Impact" is deprecated; the recommended term is "Electron Ionisation" (EI)."

Answer to Reviewer: Terms relating to mass spectrometry were possibly modified in order to meet the IUPAC recommendations.

3) "I suggest to use a slash ("/) instead of a hyphen to denote a hyphenated technique, such as, for example, TD/GC/MS."

Answer to Reviewer: Hyphens were replaced with slashes to denote hyphenated techniques.

4) "Page 1154 Line 4: The composition of individual particles cannot influence the climate. Examples for unsuitable expressions: Line 17: "Close-to-real conditions"; Line 18: "method abilities""

C868

Answer to Reviewer: Line 4: The sentence was modified according to the recommendations. Lines 17 and 18: Expressions were modified.

5) "Page 1158 Line 15-18: The PTR-MS technique on itself cannot provide structural information of gas-phase compounds as it only measures  $m/z$  values of protonated molecules and fragments thereof. Specific fragmentation patterns might help to structurally characterise a compound but therefore fragmentation patterns need to be established. Overlapping isobaric isomers mostly hinder the positive identification and additional analytical techniques are required. Line 18: Wrong literature citation: Warscheid et al. (2003) did not use the PTR-MS technique."

Answer to Reviewer: Line 15-18: The paragraph was modified according to the recommendations. Line 18: The cited reference (Warscheid et al. 2003) and the related part of the sentence were removed.

6) "Page 1159 Line 9: Maybe modify the statement that the AMS technique enables a chemical characterisation of SOA. It rather provides information on bulk chemical properties."

Answer to Reviewer: The description of the AMS instrument capabilities was modified according to the recommendation.

7) "Page 1160 Line 4: Wrong word used? Other extraction techniques, more scarcely used, have been reported (instead of: Other extraction techniques, more scarcely used, can be reported)."

Answer to Reviewer: Sentence was modified according to the recommendations.

8) "Page 1160 Line 18-25: Please check the references and the conclusions. I doubt that "direct LC-soft ionisation-MS analysis" ever led to the identification of an unknown compound."

Answer to Reviewer: The term "direct" was removed from the sentence and two references were added, which illustrate the use of LC/soft ionisation-MS coupling for the

C869

detection and the identification of polar compounds in atmospheric aerosol samples. As an example, Gómez-González et al. (2008) present the structural characterisation of unknown polar compounds in ambient fine aerosol by the interpretation of MS2 and MS3 spectra after compounds separation by liquid chromatography and compounds ionisation by electrospray.

9) "Page 1163 Line 16: Maybe add "for GC/MS analysis" as not only PFBHA has been used for carbonyl compound analysis for both SOA and gas-phase samples."

Answer to Reviewer: The precision that PFBHA is the most widely used derivatisation reagent "for GC/MS analysis" was added to the sentence.

10) "Page 1165 Line 7: The meaning of this sentence is unclear."

Answer to Reviewer: The sentence was clarified.

11) "Page 1169 Line 9: Hyphenation is not correct."

Answer to Reviewer: The comment was taken into account.

12) "Page 1169 Line 14: Molecular weight has no dimensions."

Answer to Reviewer: Dimensions were removed from molecular weight.

13) "Page 1170 Line 1-5 and corresponding Figure 7: In-solution derivatisation was performed only once. This does not provide sufficient evidence about the obtained results (minimum 3 repetitions necessary). Line 11-12 and corresponding Figure 7: On-TENAX derivatisation was only performed twice. With this procedure no statistical evidence can be obtained and error bars should be removed. Line 12-17: How were the derivatisation yields calculated? I wonder about values of 205%."

Answer to Reviewer: Line 1-5 and corresponding Figure 7: The repeatability of the in-solution derivatisation with PFBHA of the tested series of carbonyl compounds was separately evaluated. Details and values were inserted page 1170 line 6 and errors bars were added in Figure 7. Line 11-12 and corresponding Figure 7: As recom-

C870

mended, errors bar for on-Tenax TA derivatisation were removed. Line 12-17: The term "derivatisation yield" was replaced by "derivatisation efficiency". The aim of this section was to compare derivatisation efficiencies of the in-solution and the on-Tenax TA derivatisation protocols. Results had revealed that, for some compounds, the derivatisation was more efficient for the on-Tenax derivatisation protocol, leading to relative derivatisation efficiencies higher than 100 %.

14) "Page 1171 Line 18: the number of significant digits should be reduced to 2 or 3 (in the case the first digit is a "1")."

Answer to Reviewer: The number of significant digits were reduced as recommended.

15) "Page 1173 Line 2: Several LC/MS methods have been published using the DNPH method and not only HPLC-UV methods are available."

Answer to Reviewer: A reference to a publication that use the DNPH method coupled to LC/MS analysis of ambient air samples, and a reference to the limits of detection presented therein, were added, page 1173 line 3.

16) "Page 1176 Line 11-13: Unclear sentence, please rephrase."

Answer to Reviewer: The sentence was clarified.

17) "Page 1177 Line 14-18: The sentences do not seem to be finished. Please revise. Line 29: Why are another sampling duration and flow rate applied? Here, the conditions were 4 h using 150 ml/min, whereas before the conditions were always 2 h with 100 ml/min . Page 1178 Line 18: Here again, the sampling conditions were changed (1 h 100 ml/min). This is confusing as also sampling conditions can significantly affect the results. Line 24-27: Sentence was already written in line 11-13."

Answer to Reviewer: Page 1177 and 1178: The comments concern the paragraph that had been moved. Please see previous authors comment titled "Missing paragraph". The paragraph has to be partially attributed to Sect. 3.2.2 "Humidity influence" on Tenax TA derivatisation with PFBHA: the sampling flow rate applied was systematically

C871

100 mL min<sup>-1</sup>. A sampling flow rate of 150 mL min<sup>-1</sup> (and a sampling time of 4h) was only applied for the preliminary test evaluating the influence on the derivatisation efficiencies, of a relative humidity of 50 % compared to a sampling performed under dry conditions. The difference of sampling flow rates between this test and other experiments cannot change the clear conclusion that moisture positively influence the derivatisation efficiencies.

18) "Page 1182 Line 11-14: This sentence is unclear; please revise."

Answer to Reviewer: The sentence was clarified.

19) "Page 1183 Line 14-15: The authors should carefully check the references. For example, Yasmeen et al. (2011) used samples from limonene photo-oxidation experiments in the presence of NO<sub>x</sub> that likely led to different product distributions compared to limonene ozonolysis."

Answer to Reviewer: The reference was removed.

20) "Page 1186 Line 24-26: it is unclear what is meant by the "recollection option" of commercial desorbers; please, provide additional explanation about this technique."

Answer to Reviewer: The "re-collection option" of commercial desorbers was better explained page 1165 line 18, section 2.2.1 ("Thermal desorption - gas chromatography / mass spectrometry system and procedures"). Page 1186 line 24-26, a reference to this section was added.

21) "Page 1188 Line 13-14: The comparison of K<sub>i</sub> values to ambient aerosol and chamber experiments that used other precursor compounds might be incorrect as they likely result in different aerosol properties. Furthermore, different sampling conditions and analytical techniques might hinder a direct comparison."

Answer to Reviewer: A discussion of the comparison of K<sub>i</sub> values estimated under different ambient and simulated conditions was inserted page 1188 line 14. As few experimental values are available, this comparison serves to underline the need of

C872

experimental  $K_i$  values, which might help to point out parameters that influence partitioning coefficients compared to semi-empirical estimations.

22) "Page 1208 Table 2: Please, revise the table. For example, MTBSTFA-derivatised functional groups instead of "MTBSTFA derivatisable functions number". Probably, the authors mean RT instead of Tr?"

Answer to Reviewer: The Table 2 was revised as recommended.

23) "Page 1212 Table 6: A lot of abbreviations are not explained; please, define abbreviations in the table (or in the main text). For example: < Id, MW d, MW not d."

Answer to Reviewer: The abbreviations was explained in the legend of the Table 6.

24) "I suggest to change some table headings; e.g. Assignment instead of "Identification", Also observed in instead of "References"."

Answer to Reviewer: Headings of Table 7 were modified as recommended.

25) "Page 1215 Table 8: For the gas and particle phase concentrations a range is given but no explanations in the text are given. Are these the variations from repetition experiments or was a statistical error estimation performed? Please, change "lod" into LOD."

Answer to Reviewer: Details on uncertainties calculation were added to the main text Sect. 4.2.3 (page 1187 line 10). The given concentration ranges correspond to the statistical uncertainties previously determined for standard calibration curves (Student t-test). "lod" was replaced by LOD.

Response to Referee #2

Major comments:

(1) "You evaluated detection limits from calibration curves and got very low limits for most of the compounds. I was wondering, how high concentrations you had in your

C873

derivatized blank samples (laboratory or field blanks), since for this low values, blanks can be important. Did you subtract the blanks? Please, give blank values in the text or add them into some table. If you did not have any blank level, mention also this in the text."

Answer to Reviewer: Laboratory blanks were tested. Only for methylglyoxal and dimethylglyoxal on quartz filters, the observed levels were significant and consequently subtracted for constructing calibration curve and estimating detection limits. Nevertheless, the quartz filter blank reproducibility was not evaluated. These details were added to the text page 1168 line 25. Besides, blanks treatment for the limonene ozonolysis experiment were also added, line 9 p 1187 and line 14 p 1187. Chamber blanks were subtracted for the quantification of each compound (cf. Table 8). Nevertheless, as the whole mass of a given compound present in the chamber participates to the partitioning of this compound, quantifications values used for partitioning coefficients calculation were not corrected from chamber blank values but only from laboratory blank values (cf. Table 9).

(2) "You did not mention anything about desorption efficiencies. These derivatized compounds have quite high molecular masses and I am not sure if they are totally desorbed from the Tenax TA tubes. Please, give some results of desorption efficiencies."

Answer to Reviewer: Available data of desorption efficiency were added page 1168 line 25. They were obtained by performing a second TD-GC/MS analysis of derivatised standard tubes and filters just after the first one. For none of the compounds tested, a signal was observed in the second analysis, suggesting a maximal desorption efficiency under our desorption conditions. We are aware that desorption efficiencies have to be estimated by comparing thermal desorption to liquid injection. This approach was attempted. However, no relevant results have been obtained as the split ratio applied for the two methods were not comparable. In our point of view, as no signal was observed in the second analysis of a sample and as we obtained reproducible results, the knowledge of precise desorption efficiencies was not crucial. The calibra-

C874

tion curves were indeed also performed by TD-GC/MS analysis of derivatised standard Tenax TA tubes and filters. Furthermore, derivatisation enhances GC/MS analysis but also desorption efficiency by reducing compound polarity and/or increasing volatility, in spite of relatively high molecular weights.

Minor comments:

"There were lots of small corrections to the text, but I am not listing them here, since they were already mentioned by the other reviewer. However, I recommend you to go through carefully whole text and try to correct, clarify and compress it."

Answer to Reviewer: Comment was, as much as possible, taken into account.

Other modifications made in the revised version of the submitted manuscript:

- The text corresponding to the section 3.2.2 was added and the lines 19 page 1177 to 28 page 1178 were removed (cf. previous Authors comment titled "Missing paragraph" for details).

- The Table 4 was added as it was not inserted in the published AMTD version. As a consequence, previous Table 4 became Table 5, previous Table 5 became Table 6, previous Table 6 became Table 7. Other table numbers (1, 2, 3, 8 and 9) remain unchanged.

- Page 1216 Table 9: The uncertainties on experimental partitioning coefficients were not calculated correctly. As a consequence, they were recalculated and modified in Table 9. Please see the supplement to this final authors response for details.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/5/C865/2012/amtd-5-C865-2012-supplement.pdf>

---

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 1153, 2012.

C875