**Atmospheric
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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.

Anonymous Referee #1

Received and published: 4 March 2012

General comments:

The manuscript by Rossignol et al. describes a method for the analysis of carbonyl compounds, carboxylic acids and compounds bearing hydroxyl groups using multiple derivatisation techniques. Gaseous compounds are trapped and sampled using an on-TENAX derivatisation technique, while particle-phase compounds are sampled on filters and derivatised afterwards. All methods are based on thermal desorption GC/MS and provide a powerful tool for the molecular characterisation of oxidation products in both the gas and particle phase without labour-intensive extraction methods. The tech-

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nique was evaluated against a range of atmospheric relevant compounds and was applied to a limonene ozonolysis study performed in an aerosol chamber experiment. Overall, the manuscript contains a wealth of analytical information that will undoubtedly be very useful for the scientific community. However, the English usage of the manuscript is rather poor. Several sentences lack clarity and often one has to guess what the authors want to say. Therefore, a detailed review of the scientific content is very difficult at this stage and a re-review will be necessary. Furthermore, some methodological approaches are inconsistent and require a better description or discussion. Technical corrections and suggestions for improvement of the main text will be provided in a separate document.

Major comments:

(1) The authors should thoroughly revise the manuscript with respect to the English 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).

For example: Table 1

2-ethylbutanal (instead of 2-EthylButanal)

t-butyl 4-hydroxybutyrate (instead of Tert-Butyl-4-Hydroxy Butyrate)

(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 fil-

ters 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 Ki values and that the determined Ki values in this study represent the best estimates under the conditions applied.

(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.

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.

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).

Example: the term "Electron Impact" is deprecated; the recommended term is "Electron Ionisation" (EI).

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

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"

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 charaterise 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.

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.

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).

8) 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.

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.

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

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

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

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%.

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").

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

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

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 conditons 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.

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

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 NOx that likely led to different product distributions compared to limonene ozonolysis.

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20) Page 1186 Line 24026: it is unclear what is meant by the "recollection option" of commercial desorbers; please, provide additional explanation about this technique.

21) Page 1188 Line 13-14: The comparison of Ki 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.

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?

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.

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

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.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/5/C134/2012/amtd-5-C134-2012-supplement.pdf

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