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Comment

Interactive comment on “Hyphenation of a EC / OC thermal-optical carbon analyzer to photo ionization time-of-flight mass spectrometry: a new off-line aerosol mass spectrometric approach for characterization of primary and secondary particulate matter” by J. Diab et al.

J. Diab et al.

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At first, we thank the reviewer for the remarks, which helped to increase the quality of the paper.

Reviewer comments:

General remarks:

C513

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The ABC publication described a first feasibility study of the newly hyphenated analytical system. This manuscript depicts a more detailed study of several applications of the analytical method, offering also more details of the consequential usage of the analytical tool. Therefore, the present study presents new application fields such as smoke chamber aerosols and a more detailed discussion of ambient samples and wood combustion aerosol. Moreover, the previous publication focused almost exclusively on resonance-enhanced multiphoton ionization (REMPI)-MS, in the present study also single photon ionization (SPI)-MS is extensively featured. This enhances the scope of detectable compound classes considerably.

1) The manuscript should be submitted as a technique note after revision.

Response: This is fine for us.

2) The manuscript title should be re-considered. In the current title, the phrase that “a new off-line aerosol mass spectrometric approach” makes the readers misunderstand that the hyphenated EC/OC-PI-TOFMS system is developed by this study

Response: The title could be changed to: “Hyphenation of a EC/OC thermal-optical carbon analyzer to photo ionization time-of-flight mass spectrometry: an off-line aerosol mass spectrometric approach for characterization of primary and secondary particulate matter”

3) I am afraid that advantages of the hyphenated EC/OC-PI-TOFMS system are exaggerated. First, in addition to the composition/source of carbonaceous components, evolution of particulate carbon during the thermal-optical analysis is also influenced by the co-existing inorganic species such as minerals and trace metals. Second, pyrolysis OC, which is typically evolved off the filter during the EC1 step, can contribute significantly to total OC defined by the thermal-optical method (e.g., Chow et al., Comparison of IMPROVE and NIOSH carbon measurements, *Aerosol Sci. Tech.*, 34, 23-34, 2001). The authors are suggested to add a paragraph discussing limitations of the hyphenated EC/OC-PI-TOFMS technique, and meanwhile, tone down the statements

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about advantages of the technique.

Response: We cannot give information on minerals and trace elements, since these species have not been measured in the framework of this study. We focused on the investigation of organic signatures of the samples. The charring OC, which could false be assigned to EC1, should be corrected by the laser transmission and reflectance measurement of the carbon analyzer. Additional paragraph discussing limitations could be added: "The limitations in the carbon measurements lie in the distinction between OC and EC. It is highly dependable on the laser correction method and the utilized carrier gas system as well as the temperature protocol. Due to the unit mass resolution of the mass spectrometer, an assignment of compounds to the measured m/z ratios can only be taking into account the unique properties of the ionization technique (selectivity, ionization efficiency) and literature data as well as own experimental experience from previous studies, the latter also comprising chromatographic analyses to confirm assignments ." The statements about the advantages of the system can be attenuated to a certain extent, however, we are convinced that the hyphenated system contributes beneficial information about the organic content of carbonaceous fractions and in general is a helpful tool for characterization of particulate matter.

Page 272, Line 22, a right parenthesis is missing after "Nuclear magnetic resonance NMR".

Response: Thanks for the hint, the parenthesis will be added

Page 272, Line 26, a right parenthesis is missing after "LDI"

Response: This parenthesis will also be added

Page 281, Line 3 to 5, The authors should be careful about the statement that "In the OC4 and EC steps, a negligible amount of gaseous species evolve because almost all organic species have been released during the first three OC fractions".

Response: The sentence could be changed to "In the OC4 and EC steps, a negligible

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amount of gaseous species was detected. This leads to the assumption that almost all organic species have been released with the first three OC fractions.”

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