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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Functional group composition of ambient and source organic aerosols determined by tandem mass spectrometry" *by* J. Dron et al.

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Reply to Anonymous Referee n°1

We thank anonymous referee 1 for the useful comments and suggestions.

Specific comments

1- In the light of the both referees comments and of the reference indicated by referee n°2 (Russel et al., 2009), we will modify the following part of the sentence, "and difficulties in separating carbonyls from other carboxylics" (p.9255, lines 25-26). This section was indeed not updated. Sorry for this oversight. References cited by ref-

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eree n°2 (Russel et al. 2009, Liu et al. 2009) will be added and the text updated in consequence.

2- Calibration and quantification procedure of the analytical methods will be developed in section 2.2. (p.9259, line 13) as follow: "As the fragmentation is affected by the molecular structure of each compound, the calibration is based on reference mixtures containing 16 (nitro groups), 24 (carbonyl groups) or 31 (carboxylic groups) compounds of various chemical structures and including mono and poly functional molecules (Dron et al. 2007, Dron et al. 2008a, Dron et al. 2008b). For each functional group, 25 reference mixtures of equal total concentrations in terms of functional groups were analysed. For each of these mixtures, the individual compound concentrations were determined randomly. The relative standard deviations (RSD) of the responses of the different calibration mixtures were in the range 10-20 %. This particular calibration procedure involving a statistical analysis of reference mixtures attested its reliability when applied to complex mixtures." A specific paper dedicated to matrix effects and interferences for this new functional group analyse approach is currently under preparation. Some insights can be found in Dron (2008, in French). Consequently we prefer not to develop further these aspects in the present paper. We show that for the functions under study the matrix effects are not significant as far as the extracts are not too concentrated. Consequently each extract are diluted in order too minimize these artefacts. A sentence will be added in the text to point out this aspect.

3- The authors will add the reference "Calvert et al. 2002" (p.9264, line 26).

4- We totally agree with this comment and the direct relation between low carbonyl content and a minor SOA contribution suggested by the sentence (p. 9265, lines 21-22) is indeed a misleading shortcut. We also agree that only a single reaction system was studied for SOA, and it is clear that this is insufficient to draw any conclusions. The text (p. 9265 line 22) will be modified as follows: The relatively low carbonyl content found in 20 Chamonix OA compared to the high carbonyl functionalisation rates measured for the photooxidation experiments (6 to 11%) supports the assumption that the Chamonix

ACPD

10, C4933–C4936, 2010

winter OA is mainly of primary origin, if we consider the abundance of carbonyl as a marker for SOA. In a recent study conduced at Mexico City, FTIR functional groups analyses have pointed out low functionalisation rates for carbonyl (0 to 1.5%) (Liu et al, 2009) whereas SOA, mainly from biogenic origin, was a major fraction of OA (Stone et al, 2008; Hodzic et al, 2009). This result suggests that carbonyl abundance can not be considered as an univocal marker of SOA. It highlights the strong need to complete the functional group fingerprints database with other SOA precursor (particularly biogenic VOC) and, most probably, that the chemical nature of OA can not be summarized by only first generation oxidation products especially in highly photochemically active environments..

Hodzic, A., Jimenez, J. L., Madronich, S., Aiken, A. C., Bessagnet, B., Curci, G., Fast, J., Lamarque, J.-F., Onasch, T. B., Roux, G., Schauer, J. J., Stone, E. A., and Ulbrich, I. M.: Modeling organic aerosols during MILAGRO: importance of biogenic secondary organic aerosols, Atmos. Chem. Phys., 9, 6949-6981, 2009.

Stone, E. A., Snyder, D. C., Sheesley, R. J., Sullivan, A. P., Weber, R. J., and Schauer, J. J.: Source apportionment of fine organic aerosol in Mexico City during the MILAGRO experiment 2006, Atmos. Chem. Phys., 8, 1249-1259, 2008.

5- The concern of this conclusion is rather the wood combustion predominance. Also, the authors agree that the expression “rather consistent results” (p. 9269 line 28) may be misleading. The authors propose to change the sentence to (p. 9269, lines 28-29), “(. . .) rather consistent results with the organic markers approach when estimating the wood combustion contribution.”

Technical corrections

1- “rod” will be changed to “tube”.

2- Authors agree with this remark. Then, the definition of the functionalisation rates will be transferred from p. 9262 lines 12-15 to p. 9260 line 27. Also, an introducing

ACPD

10, C4933–C4936, 2010

sentence may be added before that definition such as, “It may be interesting to express the functional group concentrations as functionalisation rates.”

3- “solvents” will be changed to “solvent”.

4- “plain lines” will be changed to “solid curves”.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 9253, 2010.