Atmos. Chem. Phys. Discuss., 5, S1028–S1033, 2005
www.atmos-chem-phys.org/acpd/5/S1028/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of high molecular weight compounds in urban atmospheric particles" *by* V. Samburova et al.

V. Samburova et al.

Received and published: 2 June 2005

We would like to thank the two anonymous reviewers and G. Kiss for their helpful comments and suggestions to improve the manuscript.

Referee 1

1. Limitations of the MS method: multiply charging of ions is not a likely process in LDI/MALDI, but rather in electrospray ionization. Thus this artifact can be largely excluded for our study. This is now mentioned on p. 6.

2. Fragmentation during MS: Several experiments were performed to assure that fragmentation is likely not a serious problem. This is now emphasized in detail on p. 5-6.

3. Uncertainties of SEC calibration: We are aware of the difficulties concerning molec-

ular size calibration with SEC (see Figure 3 and corresponding discussion). However, by comparing SEC with (MA)LDI-MS we increase the reliability of the SEC size determination. This is emphasized and discussed on p. 9. In addition we would like to emphasize that we show here for the first time a comparison of two totally different techniques (SEC and (MA)LDI-MS) to determine the molecular size distribution of HULIS.

4. More references as suggested were added to the introduction.

5. As mentioned above, care was taken during (MA)LDI-MS to prevent fragmentation as described on p. 5-6.

6. Similarities to the studies of Tolocka (2004) and Kalberer (2004): We only describe the similarities of the MS from the ambient and laboratory generated samples with respect to the observed repetitive units of m/z14 and 16. We do not speculate on the specific chemical nature of the high molecular weight compounds measured in the ambient samples. We emphasize this now more clearly on p. 9. In Kalberer (2004) we discuss acetals as only one possible formation mechanism and point out that also other reaction mechanisms are likely.

7. Co-elution of HULIS and inorganic ions: We added a section about possible interferences of HULIS with important inorganic ions (nitrate and sulfate) on p. 10. Nitrate is not interfering with HULIS because it has a different retention time. Sulfate is co-eluting with HULIS, however, it is essentially not absorbing at 240nm at concentrations measured in daily samples from the same location and time ($<$ 5μg/m3). Thus the major inorganic ions do not significantly contribute to the observed UV absorbance.

8. Problematic use of humic substances as quantification standard: we agree and are aware that comparing a standard and an analyte with unknown chromophores gives rise to large uncertainties. However, as long as the chemical structure of HULIS remains unknown we see no alternative. We reanalyzed all data using Suwannee Fulvic acid (SRFA) standard form the IHSS. We discuss in detail the potential problems

associated with the quantification on p. 10-11 and clearly state that all quantitative numbers are “fulvic acid equivalents”.

9. The comparison of our data with the C-14 results form Szidat (2004) was deleted as suggested by the reviewer.

Referee 2 (G. Kiss)

1. Uncertainties on MW and concentration estimations: systematic errors about the molecular weight determinations are discussed in detail on p. 5-6 and 10-11.

2. The typos are corrected.

3. We do not cite Krivácsy (2000) with respect to the extraction procedure but only with respect to the eluent composition used for the liquid chromatography.

4. The choice of the eluent composition is now explained in more detail on p. 4 as suggested by the referee.

5. We do not use PMA and PEG as size calibration compounds, only PMA (see p. 8). The fact the not the whole elutable OC can be size calibrated with PMA is due to the large chemical variety of compounds present in organic aerosol, which cannot be simulated by one single standard. Thus there will never be one standard to calibrate all OC components in HULIS. PMA was selected for size calibration only of the water soluble (and thus polar) high molecular weight mass fraction of the total OC due to theoretical reasons and the reasonably good correlation with (MA)LDI-MS.

6. The names of the dicarboxylic acids are mentioned now on p. 7 as suggested by the reviewer.

7. Potential (MA)LDI-MS artifacts are discussed are discussed on p. 5-6 and 9 as described in the answer to referee 1 (point 1-3).

8. Additional Figures (Fig. 1a/b, discussion p. 5-6) were added showing that LDI-MS and MALDI-MS of the same HULIS sample do not differ significantly. The same was

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found for SRFA. Not all atmospheric samples are equally sensitive to matrix addition when measured with laser -MS. Addition of matrix analyzing secondary organic aerosol generated from 1,3,5-trimethylbenzene in a smog chamber was not necessary to get high signal intensities up to 1000 Da (Kalberer et al., 2004, Science). However, for the analysis of secondary organic aerosol from α-pinene and for pure surrogate standards the addition of graphite or TiN as inorganic matrices was needed to obtain measurable signal intensities. For these samples, as for HULIS, the addition of matrix did not result in a shift of the overall mass distribution (Kalberer et al., 2005, in preparation).

9. LDI-MS parameters: these were optimized as now more clearly pointed out on p. 5.

10. Limited use of AHA for quantification: As discussed in the reply for reviewer 1 (pt. 8) limitations of the concentration determination are discussed in detail on p. 10-11. Due to this limitations the concentrations given are clearly stated as “FA equivalent” masses (p. 11 and Table 1). Collection of different OC fractions for weight determination of the different fractions as suggested would not be possible with an analytical column as used here, due to the small amount of sample separable on such columns.

11. Correction done as suggested in the references.

12. The wavelength used to acquire the chromatogram is now mentioned on p. 7 and in the Figure Captions of Figure 2.

Referee 3

1. The interferences of inorganic anions (in Switzerland mostly nitrate and sulfate) are discussed on p. 10. The separation of low and high molecular weight organic compounds is performed with SEC, clearly stated now on p. 7. 2./3 We are aware of the study of Mugo and Bottero (RCM, 2004). The mass spectra shown in this paper show indeed differences between LDI and MALDI with higher mass for MALDI of a few isolated peaks up to 1800m/z and the most intense peaks between 1300-1400m/z. In

contrast, in our measurements of HULIS no significant differences are visible between LDI and MALDI and most additional peaks visible in the MALDI spectrum are due to matrix peaks (see Figure 1a/b and p.5-6). Not all atmospheric samples are equally sensitive to matrix addition when measured with laser -MS. Addition of matrix analyzing secondary organic aerosol generated from 1,3,5-trimethylbenzene in a smog chamber was not necessary to get high signal intensities up to 1000 Da (Kalberer et al., 2004, Science). However, for the analysis of secondary organic aerosol from α-pinene and for pure surrogate standards the addition of graphite or TiN as inorganic matrices was needed to obtain measurable signal intensities. For these samples, as for HULIS, the addition of matrix did not result in a shift of the overall mass distribution (Kalberer et al., 2005, in preparation). The fact that Mugo an Bottero observed differences between LDI and MALDI for fulvic acid but for our HULIS samples such differences could not be observed is likely due to the different chemical composition as described on p.6. In addition, the molecular weight range found for HULIS in our study compares well with the HULIS mass spectra measured with ESI-MS by Kiss et al. (2003) as described on p. 9.

4. We forgot to mention that we performed our measurements with AHA sodium salt, which is completely soluble. However, we reanalyzed all our data using Suwannee River Fulvic Acid Standard (SRFA) from the IHSS. Thus all comments in pt. 4 are not applicable anymore.

5. As described on p. 5-6 and in Figure 1a/b there are no significant differences between LDI and MALDI for HULIS, the focus of this paper. A careful analysis of HA (a mixture of compounds similar in complexity but different in composition, if compared with HULIS) with laser MS methods would require intensive method development and is beyond the scope of this paper. See also comment to pt. 2./3. considering laser-MS analyses of different aerosol samples.

6. We are aware of the problems SEC is posing in HULIS analysis. A main point of the paper is to demonstrate these limitations but also to overcome them (partially) by

comparing the results with LDI and MALDI-MS. We chose PMA instead of PSS as a size standard because only a very limited number of PSS standards are available in the relevant size range (smaller 4000Da), not sufficient for a reliable calibration curve. As Perminova et al. (1998) show, PMA and PSS calibration curves are similar. This is discussed on p. 7-8 in detail.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 437, 2005.