Atmos. Meas. Tech. Discuss., 6, C2332–C2334, 2013
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Atmospheric Measurement Techniques Discussions
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Interactive comment on "Application of high resolution Chemical Ionization Mass Spectrometry (CI-ToFMS) to study SOA composition: focus on formation of oxygenated species via aqueous phase processing" *by* D. Aljawhary et al.

Anonymous Referee #2

Received and published: 2 September 2013

This manuscript describes the use of an aerosol-HRToF-CIMS (a high resolution time of flight chemical ionization mass spectrometer used to analyze aerosol composition) to analyze the composition of secondary organic aerosol formed via aqueous phase oxidation. Three different chemical reagent ions are used: water clusters, iodide (clustered with water) and acetate. The HRToF-CIMS is a relatively new instrument, and the set-up described in this manuscript used to measure particle composition is unique. In addition, analyzing the same aerosol with different reagent ions is interesting and the results are important and relevant to the research community. Thus, the results

presented in the manuscript are scientifically important and well within the scope of Atmospheric Measurement Techniques. The paper is generally well written, and I recommend publication in AMT after my comments below, as well as the comments of Anonymous Referee # 1 (with which I agree) have been addressed.

1. Abstract: "In the bulk O/C and H/C space, i.e. in a Van Krevelen plot, there is a remarkable agreement in both absolute magnitude and oxidation trajectory between CI-ToFMS data and those from a high resolution aerosol mass spectrometer (HR-AMS). This indicates that the CI-ToFMS data captures much of the chemical change occurring in the particle and that gas phase species, which are not detected by the HR-AMS, do not dominate the overall ion signal."

The bulk elemental ratios (O/C and H/C) referred to here are averages weighted by the ion intensity (section 3.2.2). As shown from the calibration experiments presented in this manuscript (section 3.1), the sensitivity of the instrument to different organic species can differ by orders of magnitude. Thus, the intensity averaged elemental ratios could be significantly different from mass or mole-averaged elemental ratios. Thus, the comparison of elemental ratios from the HRToF-CIMS and HR-AMS is not rigorous, and it is not clear whether scientific conclusions can or should be drawn from such a comparison (e.g. that the gas phase species do not dominate the ion signal). This issue should be discussed in the revised manuscript.

2. Pg. 6163, lines 11-12: "Peaks higher than 300 u cannot be unambiguously assigned for the $(H_2O)_nH^+$, $CH_3C(O)O^-$ reagent ions."

The authors seem to imply that peaks lower than 300 amu can be unambiguously assigned. Considering the quantity of peaks identified some of the mass spectra must be quite crowded, and it is not clear that the peaks could be unambiguously identified. The authors should comment on this and perhaps show a figure or two – one in which the peaks can; another in which they cannot be unambiguously identified.

3. Pg. 6163, lines 15-18 : "Elements other than C, H and O were not considered in

the formula predictions as it was assumed that those elements were absent from the reagents (WSOC and H_2O_2) and purified water."

This assumption implies that there was no contamination in this system, which is unlikely for any experimental system. Purified water is often not as pure as one might expect. Especially since the HRToF-CIMS has such different sensitivities to different ions, low levels of contamination can result in significant peaks. I worry that some of these peaks may have been erroneously attributed to an organic species of a similar molecular mass. One way to check this is to conduct a control experiment – purified water, H_2O_2 and UV lights – and comment on the resulting mass spectrum in the HRToF-CIMS.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 6147, 2013.