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Interactive comment on “Analysis of the chemical composition of organic aerosol at the Mt. Sonnblick observatory using a novel high mass resolution thermal-desorption proton-transfer-reaction mass-spectrometer (hr-TD-PTR-MS)” by R. Holzinger et al.

Anonymous Referee #1

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This manuscript describes the first deployment of a novel proton transfer reaction mass spectrometer (PTRMS) for the measurement of the chemical composition of organic aerosol (OA) in the ambient atmosphere. The technique described is certainly highly promising, and the measurements seem sound. The paper itself is highly technical, providing far more detail about the instrument and data analysis than about the results (composition of organic aerosol). Given the richness of the dataset, it seems that much more could be learned about OA chemistry than is currently in the manuscript; however,

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including additional discussion risks making the paper too long and unwieldy. Thus the paper is suitable for publication, once the changes discussed below are made.

I think the paper would be greatly improved by more introduction to proton mass spectrometry. The details, strengths, and shortcomings of PTRMS are never discussed. While these are in the previous instrument paper, they should still be discussed briefly here for context. Someone new to the field would have no idea of what the technique is, or what sort of information it provides that other techniques do not. (A short comparison with AMS or filter sampling would be quite helpful.) On the other hand, potential weaknesses are not provided either. Most importantly, ion fragmentation, a very important process for understanding and interpreting PTRMS data, is not even mentioned until near the end of the paper. The lack of detection of (small) alkanes is never discussed. How do these issues affect the data analysis, and comparison to other techniques?

My other major comment is that instrumental or data analysis details are often lacking, and/or the explanations given are often confusing. This is a problem given the highly technical nature of the manuscript. Listed below are specific points/comments that should be addressed.

13974, lines 14-15: this sentence needs to be changed; filters definitely can affect concentrations of semivolatiles in the gas phase (positive or negative artifacts).

13975, line 23 (and throughout the paper): the authors should be careful not to refer to measured ions as “compounds”. This is not just semantics, given the likely importance of isomers, ion fragmentation, pyrolytic decomposition of species, etc.

13980, line 3: what are the formulae at these two masses?

13981 line 6: This sentence is very confusing – the nature of these mass errors is not at all clear. Do these errors occur on a per-extraction basis? Is there drift over seconds/minutes/hours? Why was this correction done on the mDa (mass) scale rather than the TOF (time) scale?

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13981, line 22 and Figure 5: My understanding of the text is that the hydrocarbon peaks were mostly in the background rather than in the aerosol. Is this the case? If so, this should be made clear in the caption for figure 5.

13982, line 5: why is the resolving power (3500-4000) lower than that stated for the ToF (6000)? Is this in “V mode” or “W mode”?

13982, lines 21-26: the explanation here is clear but very qualitative. This section needs an equation showing all these different terms.

13982, lines 21-26: how does ion (or pyrolytic) fragmentation affect the calculation of mass concentration? Since neutrals aren't measured, could fragmentation lead to an underestimate of OA mass? (And could it also affect elemental ratios, as described below?)

13983, line 12: is this stated accuracy for the mass concentration of a single ion, or for all ions in the sample??

Fig 7: The time series for these ions is difficult to interpret. What would be much more useful is showing the subtraction of some (averaged) data at a given nominal m/z value and given time. The residuals would then give a good sense of how good the fit is.

13987 lines 2-7: Could this “memory effect” simply result from recondensation of evaporated species, which then appear in the blanks? (As is pointed out earlier, the transfer line is cooler than the CTD.)

13988, line 11: recondensation/delayed evaporation could explain this effect as well.

13989, line 16: O/C is introduced here, but it should be mentioned it's for the measured ions, and not the whole aerosol, given all the caveats on page 13990.

13990, line 9: there are many more fragmentation-related biases than just loss of H₂O. The loss of any other oxygen-containing fragment could also lead to biases (likely negative biases, given that oxygen does not like to take on positive charge).

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13991, lines 1-5: Low loadings could simply imply that less volatile organics, which are more likely to be oxygenated, partition into the aerosol phase. Explaining this effect in terms of aging requires additional evidence, probably from other measurements.

13992, lines 12-17: an alternative explanation is that there exists exceedingly low volatility compounds with high C number.

13992, line 26: the implication of this sentence is that the compounds desorbing at the highest temperatures are less volatile than semivolatiles (“nonvolatiles”). But the term “semivolatile” covers a very wide range of vapor pressures [Donahue, ES&T 2006]. Do the authors have data correlating volatility and desorption temperatures for standards? If not, this seems preliminary.

13993, line 8: if a significant fraction of OC in the OC/EC instrument also undergoes charring, the underestimate of organic carbon could be much larger than 25%.

13993, line 18-21: Such errors in the filter measurements (positive or negative) might also occur in the filter blanks of the PTR.

Minor comments

13971 line 3: clouds->cloud

section 2.1: this section would be much clearer with an accompanying figure.

13983, line 14: I’m not clear on the intended meaning of the word “junks.”

13990, line 17: Aitken->Aiken

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