

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.

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General comment:

We thank both reviewers for their considerate and valuable comments. While the importance of our results and the high potential of the new technique are acknowledged, both reviewers found the necessary technical descriptions hard to follow and rather obscuring the results. Reviewer 1 suggests a more general introduction to PTR-MS while

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reviewer 2 suggests to remove large parts of the technical section and to provide this as supplementary information. We understand both requests but we feel that the technical descriptions are a necessary and indispensable part of this work. We decided to put most information of section 3 (data analysis) to appendices. The reorganization of our manuscript has 3 major advantages: (i) the reader does not need to work through an extensive data analysis section before he/she comes to the results; (ii) room for an extended discussion of PTRMS (as requested by reviewer 1) becomes available, and (iii) the information from the data analysis section remains an integral part of the manuscript.

In the Following we give point to point replies to the referee comments (for better readability we reproduce the comments here in brackets):

Reviewer 1:

[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. (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?]

We do not discuss the lack of detection of small alkanes because these are not expected to be aerosol constituents. The rest of the requested discussion is included. Following text has been added to the 'Instrument description' section:

“The use of PTR-MS as detector for aerosol compounds is highly advantageous for the following reasons: (i) PTR-MS is a relatively soft ionization technique; many compounds do not fragment and are detected at their protonated mass (molecular weight +1). If fragmentation occurs it often follows a well-defined pattern such as the loss

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of an H₂O fragment in the case of higher alcohols. (ii) PTR-MS is very sensitive and therefore low detection limits in aerosol analysis can be achieved. (iii) Virtually all compounds constituting the “organic carbon” fraction in aerosols can be detected, and (iv) although compounds are only identified by their mass to charge ratio in the mass spectrometer they can still be quantified at the ~30% accuracy level because of the well-defined conditions in the drift tube and the fact that proton-transfer reaction rates are usually close to the ion-molecule collision rate when a reaction is energetically possible. Using PTR-MS as detector for aerosol compounds it is possible to directly measure and quantify the total amount of organic aerosol; however, some reservations remain with respect to fragmentation. Especially alkanes and alkenes have been shown to produce relative low molecular weight fragments upon protonation (Jobson et al., 2005) and therefore a large mass fraction of such compounds remains neutral and thus undetected.”

“While state of the art online/in situ aerosol techniques such as aerosol mass spectrometry (AMS, Jayne et al., 2000) and thermal desorption aerosol gas chromatography (TAG, Williams et al., 2006) have contributed a great deal to the current understanding of aerosol sources and processing, the TD-PTR-MS instrument has genuine advantages that warrant pursuing this technique. Although TAG and TD-PTR-MS rely on the same technology for aerosol sampling, the TAG provides no thermogram information because all aerosol components are released at once into the GC column. Furthermore gas chromatography is a rather selective detector that resolves probably less than 10% of the total organic burden. AMS on the other hand, features fast and size resolved aerosol measurements. However, the technique relies on electron ionization which causes extensive fragmentation of aerosol compounds and much of the chemical information is thus lost. Both, AMS and TAG, rely on aerosol standards for quantification of their respective signals.”

“The enhanced chemical speciation allows for direct measurement of atomic O/C and N/C ratios. Again some reservations remain with respect to fragmentation because

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these ratios can be biased if e.g. the undetected, neutral fragments contain disproportionately more oxygen atoms.”

[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).]

The text has been changed: “While particles are removed by the Teflon filter, gas phase compounds should be less affected. This way contamination from semivolatile gas phase compounds on the aerosol measurement can be corrected for, although some artifacts may still persist.”

[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.]

Done. We use a clear language in the revised MS.

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

The information is now given: “. . . masses 29.998 (NO+) and 286.973 (unidentified contamination). . .”

[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?]

We replaced this sentence by following explanation which is more to the point: “Considering a mass resolution of 5000, the width of ion signals detected at masses 100, 200, and 300 Da is 20, 40, and 60 mDa, respectively. Because of this typical broadness the center of the peak could not always be determined at sub-mDa accuracy levels. This holds particularly for higher mass numbers and low intensity signals.”

[13981, line 22 and Figure 5: My understanding of the text is that the hydrocarbon

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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.]

Done

[13982, line 5: why is the resolving power (3500-5000) lower than that stated for the ToF (6000)? Is this in "V mode" or "W mode"?)

3500-5000 are the realistic (real) values under field conditions during the campaign, whereas 6000 is the specified value. Both are for V-mode operation. We clarified this in the text.

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

We refer to Holzinger et al. 2010 for a detailed description on how to calculate mixing ratios from instrumental parameters and ion signals. After some consideration we prefer not to reproduce more details of the procedure here.

[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?)]

Yes. (Yes.) Both these potential issues are now discussed in the experimental section.

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

This is the estimated accuracy of a single ion. We specified this in the text.

[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.]

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We think that Figure 7 (Fig. D3 in the revised MS) is a clear (qualitative) demonstration of results from the procedure to correct for overlapping signals and therefore we want to keep it in its present form. However, we improved the figure by adding a legend and by using more contrasting colors for the data series. We have also done the test suggested by the referee and it is confirmed that the procedure works flawless in the sense that the total signal is preserved on nominal m/z values.

[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.)]

No, we do not think so. It is true that species evaporating at high CTD-cell temperatures may recondense on the cooler transfer lines or the drifttube. However, in a subsequent field blank run this causes a constant memory effect which is independent of the CTD-cell temperature. Semivolatile gas phase compounds, however, will contaminate the CTD-cell during field-blank sampling and cause the observed signals during the field blank measurement.

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

We cannot think of a simple recondensation/delayed evaporation process that could explain this behavior. It is hard to understand why the field blank signal of this compound is consistently higher at high CTD cell temperatures, and we cannot think of any other plausible explanation than the one we give in the manuscript. Recondensation/delayed evaporation should cause the same high levels of contamination for the aerosol runs.

[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.]

Done

[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

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negative biases, given that oxygen does not like to take on positive charge).]

We agree. We generalized our statement which is now referring to neutral fragments in general.

[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.]

Our subsequent analysis indeed shows that during times of low aerosol loading the total burden was less volatile (see Figure 10b), which is not surprising because we also measured a higher oxygen content. The question is: why is the oxygen content higher? Since primary aerosol compounds or gas phase precursors are generally more reduced, we argue that these aerosol loadings are much more aged.

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

We agree, however we could not find any evidence of such compounds in our data, whereas we do find evidence for significant effects of charring. We added this alternative explanation to the manuscript.

[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.]

We did not want to suggest that these compounds are less volatile than “semivolatiles” as defined in Donahue et al. (EST, 2006). Instead we argue that these compounds must be less volatile than e.g. alkyl nitrated. But likely they are still within the range of semivolatiles. The text has been corrected accordingly.

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

True, but the protocols for measuring TOC, OC, and EC are optimized to reduce the effects of charring. Therefore we are confident that charring was not a significant issue for the filter analyses (see Jankowski et al., 2008).

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

Yes, such effects may indeed play a role and may cause elevated field blank signals especially during episodes with low aerosol loadings.

[Minor comments]

All corrections were done. We are not sure what kind of figure the referee would like to see in section 2.1. We decided not to include a map with the location of the observatory. Instead the coordinates of the observatory are given and it is easy enough to retrieve a map from other resources.

Reviewer 2:

[My recommendation would be to sharpen the focus of the paper on the chemical analysis of OA and to move the specific mass-spectrometric aspects (perhaps the whole part 3) to the supplementary information.]

We found an alternative solution to this problem by putting this information into appendices. See our general comment.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 13969, 2010.