

Interactive comment on “Aerosol analysis using a Proton-Transfer-Reaction Thermo-Desorption Mass Spectrometer (PTR-TD-MS): a new approach to study processing of organic aerosols” by R. Holzinger et al.

Anonymous Referee #2

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General Comments:

This is a substantive manuscript that describes a new aerosol thermal desorption instrument that could contribute to the growing body of research into aerosol organic composition, sources, and formation mechanisms. Results from a smog chamber study of SOA formation and data from a field deployment are presented. The manuscript is generally well organized and well written, but there are a few issues I feel the authors should address prior to publication.

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Specific Comments:

1) The instrument represents a new configuration, not really a novel analytical approach. PTR-MS and collection/thermal desorption PTR-MS have previously been applied to aerosol organic composition measurements, as cited by the authors. The collection/desorption inlet is essentially that already described by Williams et al. Programmed thermal desorption with PTR-MS has been used in a laboratory setting to measure vapor pressures (Cappa et al., 2007, 2008a, 2008b).

2) The authors tend to calculate the instrumental detection limit in mass/volume units and then convert to sampled mass. This seems backward since the fundamental detection limit is a function of the sampled mass and the mass/volume detection limit is dependent on the sampling time (sampled volume).

3) The statement that many compounds are detected at their protonated mass using PTR-MS is most applicable to the lighter compounds measured in the gas phase, while larger organic molecules, such as those expected in aerosols, fragment to a significant degree. The high temperature used in the drift tube also potentially exacerbates this. The authors describe the considerable fragmentation they observed in the results section.

4) In describing the instrumental operation, there is no mention of a delay following the closing of V2 and V3 prior to opening V1. If this is so, it represents a change from the operation described by Williams et al. with the TAG instrument (to evaporate water) and would allow the authors instrument to measure semi-volatile compounds that might be missed by the TAG instrument—this might be worth considering. One might also expect a pulse of water into the drift tube during the early stages of desorption; is this observed?

5) CTD PTR-MS has previously been used for ambient measurements (Thornberry et al.)

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6) The authors assume $2e-9$ for the proton transfer reaction in the drift tube, but state that reaction rates for oxygenated compounds react at higher rates (>50% higher). Given the AMS data on O:C ratios in aerosols (as well as the general statement that aerosol organics tend to be oxidized), doesn't this uncertainty propagate through to the measurements of mixing ratios and mass balance? This is mentioned only briefly at the bottom of page 25993 and probably deserves more consideration due to its impact on quantification. What calibrations were performed to verify the instrument sensitivity and such effects as transmission?

7) The authors should consider mentioning literature on programmed thermal desorption such as Cappa et al. (2008b) and Tobias and Ziemann (2000) or similar in their discussion of the thermograms.

8) Have the authors done any tests on the effect of transfer line/drift tube temperature on the transmission/detection of compounds that evolve at higher temperatures? This would provide evidence that the lowest volatility compounds are not being lost to surfaces.

9) The y-axis in Figure 3 would be better left in signal units than converted to mixing ratios since the definition of mixing ratio is different for the gas-phase and aerosol periods.

10) It would be nice to see a longer time series plot of just the aerosol data from the measurement campaign to see the range of signals observed. And perhaps the relative ambient gas-phase to aerosol-phase mixing ratios (accounting for concentration) observed at some masses.

Technical Comments

P25988, L22: suggest deleting "also" P25992, L9: are the values of the isotope abundances (1.5% and 2.5%) in agreement with the isotope abundances seen for the parent compounds—these seem to fall outside the natural abundance range of C13 (<

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1.15%). P25995, L23: "gasphase" should be "gas-phase"

References

Cappa et al. (2007), *J. Phys. Chem. A*, 111, 3099-3109. Cappa et al. (2008a), *J. Phys. Chem. A*, 112 (17), 3959-3964. Cappa et al. (2008b), *Proc. Natl. Acad. Sci. USA*, 105, 48, 18687-19691. Tobias and Ziemann (2000), *Env. Sci. Technol.*, 34, 2105-2115.

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