

***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.***

**R. Holzinger et al.**

r.holzinger@uu.nl

Received and published: 2 February 2010

We thank both reviewers for their work and useful comments that help to improve our manuscript. Here are our point to point replies:

Referee 1:

- 1) good suggestion – done.
- 2) Corrected.

C10399

3) Included.

4) Corrected.

5) The CTD cell has indeed AMCX coating. We specified this in the text.

6) We measured liquid standards of organic acids,  $\alpha$ -pinene oxidation products and alkanes amongst others. Of the alkanes, we measured up to C<sub>24</sub> (as single compounds dissolved in chloroform) and we found 100% recovery. However, more work is still needed to fully characterize the behavior of the inlet system.

7) The statement seems plausible, however, experience shows that heating to 350°C is useful despite the cooler surfaces downstream: (i) We have not observed significant carryover or contamination. If this was a significant problem we should have observed it during the 4 weeks field campaign at the CESAR site. Probably the combination of surface coating and the low pressure in the transfer lines (a few hPa) helps avoiding re-condensation. (ii) We have observed single masses exhibiting the maximum signal around 300°C. (iii) At higher temperatures a significant fraction of volatilized matter is not in the form of original aerosol compounds but a product of combustion processes on the CTD cell; i.e. the volatilized compounds are more volatile than the original compounds. The drop around 200°C in Figure 9 is therefore not necessarily related to the temperature of the transfer lines.

8) This is a point that we now acknowledge in the revised manuscript. However for the reasons given in answer #7 the loss may be relatively minor. Following text was inserted p25988, L12: ‘Compounds that are volatilized at CTD cell temperatures above 200 °C may re-condense on the cooler transfer lines. This may lead to contamination and a substantial loss of the low-volatility fraction. So far we have not observed significant effects of re-condensation, however, the particular characteristics of this potential problem still need to be thoroughly investigated.’

9) Right. We corrected the statement.

C10400

10) Many oxygenated compounds also have rate constants around  $2\text{E-}9$  (e.g. glyoxal  $1.34\text{E-}9$ , acetic acid  $2.27\text{E-}9$ ). We slightly changed the text ('oxygenated compounds CAN react at higher rates') to avoid the impression that they exclusively react at higher rates. Therefore, using the standard rate constant seemed the only reasonable way for us to deal with such a mix of gases. The suggestion of using variable reaction rate constants based on functionality is very interesting and is maybe worth implementing in the new high mass resolution version of the instrument.

11) Oligomer formation may be responsible for signals above these thresholds. However, this process was minor in our experiments (Figure 4).

12) Reference included.

13) We are aware that our lab experiments were not set up to mimic ambient conditions. However, our data conclusively demonstrate the major differences between chamber and ambient aerosol. We think this message still needs to be communicated more clearly.

14) Changed.

15) We agree – thanks!

Referee 2:

1) We feel that our approach is different enough from previously described configurations/instruments that the term 'novel' is justified.

2) Besides mass/volume we gave the detection limit also as sampled mass because –as the referee points out – this is the more fundamental quantity.

3) We agree to the statement and we think that these points are adequately dealt with in the manuscript.

4) There is indeed no delay. Low volatility compounds can thus be detected and a (minor) water peak is observed.

C10401

5) Corrected.

6) The reaction rate constant is one of the largest uncertainties. The determination of the transmission sensitivity has been described in the MS. In addition gas and liquid standards have been measured.

7) Done.

8) We have not done extensive tests with changing the temperature of the transfer lines. It's a good suggestion to have a closer look on this. However as mentioned above (#7 Referee 1), we do not think that this was a serious limitation.

9) We improved the Figure caption and clearly specified the units.

10) The more detailed analysis of the field data is subject of an upcoming paper.

Technical comments: The isotopic abundances of 1.5% and 2.5% is higher than what is expected from the natural abundance. This is most likely due to instrumental noise and/or background contamination which contributes relatively more to the lower  $^{13}\text{C}$  signals. The 0.3% error was solely calculated from counting statistics and it does not take care of potential offsets. However the derived values are good enough to limit the numbers of carbon to 1 and 2, respectively.

---

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 25983, 2009.

C10402