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Atmospheric
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Interactive comment on "An aircraft-borne chemical ionization – ion trap mass spectrometer (CI-ITMS) for fast PAN and PPN measurements" *by* A. Roiger et al.

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We would like to thank both reviewers for the very positive comments on our manuscript. All recommended minor technical corrections will been included in the final manuscript. The reviewer 1 raised a few minor issues which we address below (for convenience these questions are repeated in bold letters).

Maybe I haven′t seen it, but I only found the isotopic calibration for mass 59, that is PAN (equation 1), but not for PPN or MPAN.

We have not applied an isotopic calibration for PPN or MPAN, but as mentioned in the "Summary and Conclusions" section, work on a calibration in the laboratory with the help of diffusion sources. To make this more clearly in the final manuscript, we changed part of Sect. 4.6.

Sect. 4.6 (p. 4336, l. 25)

from: "For the calculation of our PPN mixing ratios, we assumed the same thermal decomposition rate in the TDR and the same rate coefficient for the ion-molecule reaction with I^- as for PAN. The constant K_{aa} is calculated at 0.9662 from the terrestrial isotopic distribution (see Eq. R3)."

to: "No isotopic calibration was applied for higher homologues of PAN. However, the sensitivity for both PAN and PPN can be assumed to be identical (Slusher et al., 2004, Flocke et al., 2005b, LaFranchi et al., 2009). For the calculation of PPN, in Eq. R3 the signal at mass 59 amu is replaced by the signal at mass peak 73 amu (for calculation of ratio R). Due to the proximity of the two mass peaks (Δm/z=12), the relative mass discrimination of the ion trap can be neglected. The constant K_{aa} in this case is set to 0.9662, as calculated from the terrestrial isotopic distribution, whereas the constant K_{as} (contribution from ambient PPN on the PAN calibration peak) is negligible."

Moreover, it would be very nice to see how strongly the sensitivity changes along a flight (a figure would help) and what the main drivers for the relevant changes are.

Sensitivity changes are illustrated in Figures 5 and 6. Therefore, we decided not to include a further figure. Apart from start-up effects, there are two main reasons for sensitivity changes: 1) consecutive reactions as described in Sect. 4.2 and shown in Fig. 5, and 2) changes in water vapour mixing ratios described in Sect. 4.3.1 and illustrated in Fig. 6. We added part of this information in the section "Summary and Conclusions".

Section 5: (p. 4338, l. 5)

from: "The isotopic standard turned out to be especially important in strongly polluted air masses, because of the high reactivity of the product ion."

to: "The isotopic standard turned out to be especially important to account for the water vapour dependency of the PAN sensitivity, as well as for the high reactivity of the product ion which was especially observed in strongly polluted air masses."

You usually give the signals in "peak heights / arb. u.". This is uncommon, right? Usually counts per second are given. Then you can give the sensitivity in cps ppv-1 and the background in cps. Then the reader has the chance to follow your estimation on the accuracy, precision and detection limit. I strongly recommend improving section 3.4 and the figures in this respect.

The CIMS-method relies on ion abundance ratios and not absolute ion concentrations or absolute ion count rates. We measure ion currents using a conversion dynode, followed by a multiplier and an electrometer. The analogue ion current output of the electrometer is then digitalized and converted to a frequency, which is proportional to the rate of ion impingements on the conversion dynode. However, this frequency represents not the absolute rate of ion impingements (ion count rate). The dimension of this frequency is per second, but this frequency should not be termed ion count rate to avoid misunderstandings. To be consistent with this argumentation, we use in the final manuscript the term "relative ion count rate" (in arbitrary units).

We added this information in the final manuscript in Section 3.1, and changed the corresponding figures in this respect.

"The observed water vapour dependency is accounted for by the on-line calibration." That is, you "only" apply the isotopic calibration, which partly or even largely reflect the H_2O dependence, right?

Yes, as mentioned above, the water vapour dependency is one of the main drivers for the sensitivity changes.

Can the combination of the isotope-calibration derived sensitivity, the laboratory-measured H_2O dependency (figure 6) and H_2O data from a hygrometer onboard be used to retrieve a calibration for PPN?

Figure 6 shows already the in-flight derived H_2O dependency of the constantly added isotopic PAN standard. To point this out more clearly, we added further information in the final manuscript:

Sect. 4.3.1 (p. 4333, line 13)

"Humidity was measured with the standard Falcon meteorological measurement system including a combination of three instruments: a commercial aircraft dew point hygrometer (GE 1011B, General Eastern), a slightly modified capacitive sensor (Humicap-H,Vaisala) and a Lyman-alpha absorption instrument (Buck Research, Boulder)."

Actually, the answer to the question is yes: The H_2O dependency is captured by the actual isotopic ion signal at mass 61 amu, and this isotopic signal is used for the calculation of PPN (Eq. 3). As mentioned above, we changed the beginning of Sect. 4.6 in the final manuscript.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 4313, 2010.