

Interactive comment on “Formaldehyde measurements by Proton Transfer Reaction – Mass Spectrometry (PTR-MS): correction for humidity effects” by A. Vlasenko et al.

Anonymous Referee #3

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The manuscript describes the corrections to HCHO measurements using the PTRMS technique. Although PTRMS is in principle able to detect HCHO, H₂O respectively H₃O⁺ ions within the detection system reduce significantly the signal. The paper describes internal kinetics and a method to compensate for water in the drift tube as well as an intercomparison with the Hantzsch technique in the lab and in the field.

General remarks

It would be a good idea to be able to measure HCHO additionally with a multicomponent technique like PRMS. The data presented show that PTRMS delivers a signal that can be corrected to yield HCHO concentrations within about 15% compared to

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the Hantzsch technique. As the correction is high compared to other methods the technique is subject to uncertainties in all parameters entering the correction algorithm e.g. water concentration measurement and in the rate constants used in the kinetics. These uncertainties affect both the precision and the accuracy of the measurements. Under controlled conditions in the laboratory this seems to work (fig.4). However, under field conditions during the Egbert field study (Fig.6), the variability is by far higher. Under typical mixing ratios of a few ppb the deviations are far beyond the precision and accuracy of the Hantzsch technique. Interferences may arise from MHP methylhydroperoxide as well as from HMHP, Hydroxymethylhydroperoxide. There is nothing published about the Hantzsch technology interference but HMHP should be decomposed in the solution to $\text{CH}_2\text{O} + \text{H}_2\text{O}_2$ and affect the Hantzsch instrument as well. Also for high precision measurements Hantzsch needs a water vapour correction for the stripping coil conditions as well.

The article does not go into detail concerning detection limits and accuracy and precision and possible errors in the water vapour correction. Thus, although it is an interesting approach, in clean to moderately polluted regions with mixing ratios of 0.5 to ~ 3 ppb the techniques still seem not to be sufficient for precise measurements.

A further paragraph on error estimates would improve the paper. Although typically well readable the sentence on page 973, line 10 to 13 contains a grammar error.

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