

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

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We appreciate the positive evaluation of our combined (experimental and modeling) approach. We would like to thank Referee#1 for his/her comments.

Specific comments: One page 975 (Lines 14–26), the authors compare counts of M37 in absolute terms as well to other users and other publications. It seems like it would be more instructive to include the primary ion counts as well. The counts of any individual ion that is being monitored can significantly be influenced by the electron multiplier age and voltage. In my experience (albeit fairly limited) it's not necessarily the total ion counts of M37 that matters, but the ratio of that to M19 (or M21) to indicate the degree

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of clustering.

In this paragraph we used normalized counts of water dimer ions, i.e. $mz37/mz21$ and compared our data with the same type of signals from other reports. So from this prospective we feel that the original text contained the information that Referee#1 is asking for. Since Referee#2 pointed out that such a comparison is hampered by the fact that various PTR-MS systems have been operated under different drift tube condition we changed the text, adding a caution about the qualitative nature of the comparison.

In a few locations within the manuscript, the authors discuss the humidity of 15 hPa being critical, but then discuss H_3O^+ ion concentrations and H_2O concentrations in units of $\#/cm^3$. Somewhere in the manuscript, I think it would be useful to make a small table to indicate the total amount of water (in the same units) in the drift tube as a function of atmospheric relative humidity and at different temperatures. Both from the water source and from the atmospheric sample. Maybe also include how that could change by varying drift tube pressures. That way, this technique of correcting for humidity effects could be extended towards a wider range of meteorological conditions.

It is true that two kinds of units used to express water vapor concentration. Firstly, we use $\#/cm^3$ units because these units are more relevant and popular for drift-tube kinetic simulations (Fig.1) which illustrate the importance of $[H_2O]$ concentration. Later, we switched to hPa units since we are interested in ambient water vapor concentration and absolute humidity is usually expressed in % or hPa. There is a straight forward conversion from ambient absolute humidity (in PTR-MS sample flow) to drift-tube $[H_2O]$ according to pressure drop. We added text to give an example of the relation between $[H_2O]$ concentration, expressed in hPa and molecules/ cm^3 . Since we operated drift-tube pressure at a constant pressure with the same water flow running through ion source we are unable to add a table to indicate the total amount of water as a function of different drift pressures.

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Technical corrections: page 966 (line 19) change environment to plural and eliminate the word a

text changed accordingly

page 967 (line5) define MAX

text added

line 14 – H-HCHO+ and protonated seems redundant (since H-HCHO+ is protonated formaldehyde).

redundant word removed

line 24 - change "the" to "a" before significant. line 28 – insert "a" before the word "specially" 969 (line 1) suggest adding "as shown in reactions R2 and R3" after the word "ions"

text added

Line 16 – define reaction to which you are referring. This isn't obvious to me.

Ammonium acetate is the salt of a weak acid and a weak base and it is often used as a buffer solution. There is always some dissolved ammonia present in this solution which takes part in the Hantzsch type reaction with acetylacetone and produces a fluorescent derivative of HCHO (Fig.1 in this response)

Page 972– when simplifying reaction 1 to obtain reaction 2, I'm not sure I understand the math. The assumption in line 21 would make more sense if the approximately equal sign was replaced by a >>.

We would like to thank reviewer for noticing this misprint.

Pae 975 – line 6 – sentence starting with "Assuming" is awkward and hard to follow. Suggest combining into two sentences and clarifying the points.

The sentences were reworded.

Page 976 – line 5: hyphenate first-order Line 11 – might want to say why you monitor ion 21 and not 19 (for those unfamiliar with mass spectrometry).

Text added.

Line 21 – put the word “the” before “Hantzsich”. Page 978 – line 8: I don’t understand the phrase – “: : concentrations have of MHP have ranged...” seems like a typo or something.

Typo corrected.

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 965, 2010.

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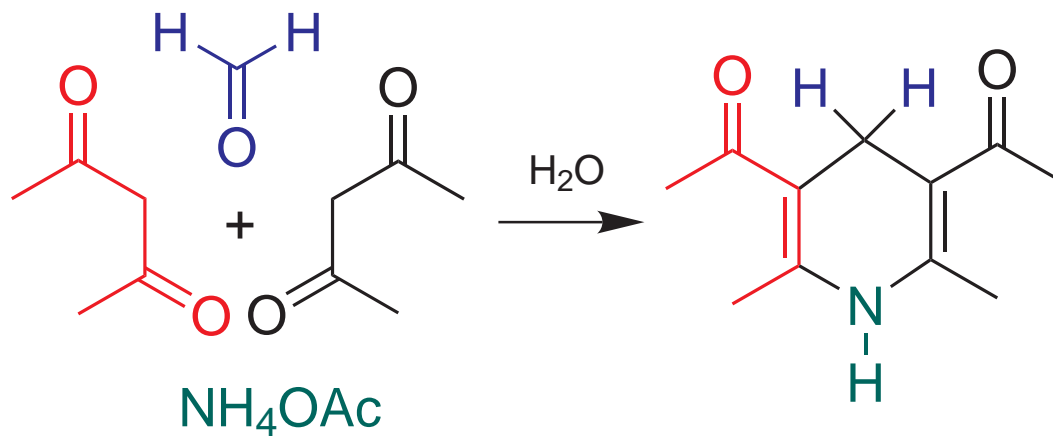


Fig. 1. Hantzsch reaction scheme

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