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

j. ortega (Referee)

ortega.john@gmail.com

Received and published: 26 April 2010

General comments: This paper describes an approach for using a commercial PTR-MS for accurately measuring atmospheric formaldehyde and accounting for relative humidity effects. This measurement has historically been difficult due to the similarity in proton affinities between water and formaldehyde. This leads to the forward and reverse reactions (protonation and de-protonation in the PTR-MS drift tube) being in competition and very sensitive to the amount of water available as a reagent. I think the paper is good and recommend publication with minor revisions. The content is appropriate for the journal, the science is sound, and the length is appropriate. Figures
are clear and adequately support the manuscript’s text.

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 of clustering.

In a few locations within the manuscript, the authors discuss the humidity of 15 hPa being critical, but then discuss H3O+ ion concentrations and H2O concentrations in units of #/cm3. 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.

Technical corrections: page 966 (line 19) change environment to plural and eliminate the word a page 967 (line 5) define MAX line 14 – H-HCHO+ and protonated seems redundant (since H-HCHO+ is protonated formaldehyde).

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

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

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). Line 21 – put the word “the” before “Hantzsch”.

Page 978 – line 8: I don’t understand the phrase – “…concentrations have of MHP have ranged...” seems like a typo or something.