Review of Validity and limitations of simple reaction kinetics to calculate concentrations of organic compounds from ion counts in PTR-MS
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Holzinger et al.

Summary:

The authors calibrated a large number of different PTR-MS instruments and used this information to derive mass-dependent transmission curves, and to evaluate a few other controls on sensitivity, including the effect of humidity. The purpose is to determine if sensitivity of a particular PTR-MS instrument to a particular VOC can be estimated, when the VOC rate constant and transmission through the instrument are known. The authors present a method for determining the transmission as a function of m/Q. Overall the expected and measured sensitivities agree quite well, if transmission is taken into account. A major remaining uncertainty is the effect of high concentrations of water cluster (H3O+(H2O)n).

Major comments:

The manuscript is improved from the previous version. The work is not particularly novel, as the effect of humidity on sensitivity and the reagent ion distribution, the mass-dependence of transmission, and recommendations for PTR operating conditions have been addressed previously in many other publications. The paper mainly focusses on transmission effects, so I am not sure that the analysis is comprehensive enough truly evaluate sensitivity calculation as promised in the title. However the number of different PTR instruments compared is unprecedented and this paper could be a useful resource for other PTR operators.

I have a few major questions:
1) Equation (1) seems to be a correction for the duty-cycle of ion extraction into the ToF region of a mass analyzer. For a ToF mass spectrometer a should be exactly equal to 0.5. Why not apply the known duty-cycle correction directly, before fitting equations (2) and (3)?

2) The purpose of the paper is to evaluate the agreement between sensitivity calculated from reaction kinetics, and measured sensitivities. Any number of things could cause measured sensitivities to deviate from expected sensitivities, including mass-dependent transmission, differences in rate constant with H3O+ vs H2O*H3O+ or larger water cluster back-reaction, fragmentation, uncertainty in rate constant, and effect of contaminant reagent ions (e.g. O2+).

The paper focuses almost exclusively on determination of mass-dependent transmission and states that quantitative detection is possible within 30%. Is the 30% uncertainty entirely attributable to difficulty in determining the transmission function? Is the largest source of error the transmission curve, reaction with water clusters, or some other effect?

Specific/minor comments:

Page 9 line 11: "We find that typically 'flatter' transmissions (smaller parameter 'a' in Eq.1) were retrieved when the instruments were (deliberately) operated at lower E/N (thin lines in Figure 3)."

This seems a little strange because Eq.1 is a function of the mass analyzer, not the drift tube – why would the drift tube conditions affect the extraction duty-cycle? (or anything downstream)? Is it that the transmission as a function of mass is not actually changed, but is rather an artifact of lower reaction rate for certain compounds used to determine the transmission curve? If so, then this suggests that

benzene etc. should be excluded from determination of the transmission curve, or that only dry air and/or high E/N should be used.

Page 13 Line 22. Likely this is because m37 is consistently transmitted with higher efficiency than m19. Therefore if most reagent ions begin their journey into the downstream optics as m37, and then at some later point decluster to produce m19, the observed m19 will be higher during humidified measurements.

Page 14 line 13: A citation is needed for this sentence: "in traditional PTR-MS applications that focus on volatile organic compounds fragmentation of compounds is the exception rather than the rule"

Figure 3: It would be much easier to compare the transmissions of various instruments if the y-axis scale were the same in each subplot.