

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:

A large number of PTR-MS instruments were calibrated using the same calibration system and gas standard cylinders. The reproducibility of the derived sensitivities is reported and compared between different instruments. Further discussion explores the effect of sample matrix and instrument operating condition on the calibration reproducibility. A method for estimating the mass-dependence of ion transmission through a PTR instrument is presented. In general it seems that PTR measurements are highly reproducible. Various instruments have different sensitivities and response to humidity, depending on instrument model and ionization technique, as expected. Mass-dependence transmission can significantly change the detected ion count rate and should be taken into consideration when calculating sensitivities of uncalibrated compounds.

This kind of intercomparison is a valuable exercise and I think these data should be available to the PTR community. The discussion of transmission curve is interesting and novel. However, on a whole the presented data and discussion are rather limited, and the paper is somewhat unfocused. The research objective stated in the title of the paper cannot be addressed without a larger number of compounds, an exploration of functional-group dependence, and assessment of the effect of fragmentation. Some important details of methods and data treatment are omitted. I can see this work as a valuable component of a larger study, for example an intercomparison of ambient data from the PICAB campaign or a more robust presentation of the transmission curve analysis. The paper would require major revisions before being publishable.

Major comments:

The purpose of the paper is a little unclear. Is it to evaluate the agreement between different PTR instruments or evaluate long-term stability? The title suggests it is to evaluate a method of determining sensitivity for uncalibrated compounds. If so, effect of fragmentation and wall-interactions should be considered.

The linear relationship between proton-transfer rate constant and sensitivity for select group of simple compounds has been reported since some time. This aspect is not particularly novel and does not require so much discussion.

The consideration of mass-dependent transmission is interesting and important for a robust calculation of sensitivity but is weakened by the very small number of compounds used to derive the curve. The degree of uncertainty in the derived transmission curve is not quantified. It would be of interest to describe how much the transmission curves vary between instruments, whether the curves can be wholly explained by known effects with ion optics, tof duty cycle, etc; and how much we can expect the transmission curve to vary in a single instrument given different instrument settings and typical campaign variability.

Specific comments:

The introduction is missing references to several highly relevant papers including methods to relate reaction kinetics to concentrations (Sekimoto et al. IJMS 2018; Cappellin et al. EST 2012, etc), a reference to the source of the kinetic rate constants In Table S3, and recent reviews that include assessments of PTR-MS precision and accuracy (e.g. Yuan et al. Chem. Rev. 2017). Additionally the introduction needs some more background about mass-dependent transmission, why it is important to consider, and previous methods used to determine the transmission curve in CIMS instrumentation. Relatedly there should be some information about the different hardware components of the system and how they're expected to affect transmission in different masses ranges; this is necessary to introduce Section 2.2.1.

Section 2: Can you please provide an overview of the instruments and the relevant differences among them?

Page 3 section 2.1 Here are missing some details about how the calibration system operates. Are the calibration compounds injected into the sample loop as pure gases, or is a pre-diluted sample of a standard cylinder collected in the sample loop and later released into a secondary dilution stream? What is the advantage of using this system compared to diluting a constant stream of calgas with known flow into a dilution stream (dynamic dilution)? What is the material of the calibration system? Were wall-loss effects considered?

Page 3 line 25: Was a comparison of the two successive calibration cylinders conducted, to ensure consistency?

Page 3 line 28: Is there any information on long-term stability of siloxanes in cylinders? Monoterpenes are known to be not especially stable long-term. When were the cylinders produced?

Fig. 2: The many subfigures and small text make this figure difficult to read and grasp the main point. Why is dry nitrogen included twice?

Eq. 1: what is $f(M)$ - the detected signal? In cps or ncps? For the time-of-flight instruments, is it corrected for the duty-cycle of the ToF extraction region? When adding together the sensitivities of fragmenting compounds, which mass is used for M : the parent mass, the fragment, or an average?

Were the forms of equations 1,2, 3 determined empirically or are these based on some knowledge of relevant ion physics?

Page 6 line 4. It would be helpful to have a figure in the main text showing an example optimized fit of Eq1, Eq2, Eq3 to the six compounds, as well as the final retrieved transmission from Eq4 compared to real data (e.g. Figure S2 as a publication-quality graphic).

Page 7: Is the effect of the much higher temperature in the drift tube (compared to ambient) on the kinetic rate constants considered?

Page 7 line 17: Not clear if normalizing factor "N" includes correction for transmission; says so in page 6 line 22 but not here?

Page 8 line 19: what is meant by "steeper" transmission?

Page 11 line 12: isn't this in contradiction to earlier statement about PTR3; the high sensitivity is due to long reaction time?

Page 13 bottom half: It is well understood that humidity affects PTR sensitivity and there are well established methods for correcting the sensitivities of conventional PTR instruments. Were corrections for humidity not applied?

Page 12 Line 29: probably because the primary ion distribution is shifted towards m/z 37, which is heavier than m/z 19 and therefore transmitted with higher efficiency

Figures 5-7: Why is PTR3 HAR not included in these figures?

Figure 6: Is the ratio of m/z 37:19 corrected for transmission effects? If not, this is not a particularly useful point of comparison, because it reflects the downstream ion optics rather than the actual conditions present in the drift tube.

Figure 6: The sensitivity of some instruments, even after normalization, seems to be quite unstable from day-to-day. Can you comment on this?

Technical corrections:

Footnotes would be better placed in the main text as part of the methods explanation.

Eq. 10; note that this is only valid if reagent ions are negligibly depleted