AMTD - 2015-251: *Characterization of the mass dependent transmission efficiency of a CIMS*

by Heinritzi et al.

Author's reply to Anonymous Referee #1:

M. Heinritzi on behalf of all author's.

We thank the referee for commenting on our manuscript. In this answer the referee's comments are shown in black Times New Roman Font, our replies are shown in blue Calibri Font.

This paper describes the determination of the mass-dependent ion transmission efficiency of a Tofwerk "APi-ToF" with and without a (nitrate) CI source. Overall, the determinations are well done, and nicely described. The mass-dependent ion transmission of a mass spectrometer is no doubt important to understand and all operators of such instrument should do such tests.

However, that does not mean each determination on an instrument should be published as stand alone papers. The main reasons being that the scientific and technical merits of this work do not extend beyond the authors' instrument, much as a calibration factor for one instrument does not apply to another. While there could be value in either reporting a new insight into what the key controls on a response function are, or describing a new method for constraining the dependencies, such new insights or methods are not presented here.

We are fully aware and state it also in our manuscript that our results are not to be directly transferred to other instruments. The importance of our manuscript lies however not in the specific results, but in the consistent description of the method for obtaining these results. This includes a description of the compounds used for depletion of the primary ions, the measurement setup as well as new and specially designed data analysis procedures. The referee states that "all operators of such instruments should do such tests" and we provide a detailed and clear description of what is necessary to do this for a nitrate based CI-APi-TOF. So our study does clearly extend beyond just our own instrument.
Currently, numerous groups are measuring ELVOCs with a nitrate based CI-APi-TOF and the transmission efficiency is a large uncertainty in quantification of these molecules. These measurements will directly affect e.g. SOA yield estimations and parametrizations of nucleation rates with respect to ELVOC concentration, which both have an effect on global modeling of aerosol radiative effects. The transmission efficiency of the nitrate based CI-APi-TOF varies in our study by a factor of 5, but for other instruments and settings this could look different. So for comparisons between different instruments as well as for better quantifying ELVOC effects on aerosols and climate it is crucial that the CI-APi-TOF community knows about ways to estimate the transmission efficiency and a consistent best practice procedure is applied. So far the only way of getting an idea of the transmission of a nitrate based CI-APi-TOF was the High Resolution DMA method (described by Junninen et al, 2010). As we discuss in our paper, this method does not include transmission effects of the ion source itself. As we found in our study, these effects are not negligible. So our improved depletion method enables us and other users for the first time to measure the transmission of the instrument in the exact same state as during standard measurements. Furthermore, the exact choice of the compounds used for the depletion/titration experiments is of interest, as it is important to find a set of compounds that cover the entire mass range.

I acknowledge that applying some of the methods used herein to a nitrate CI APi-Tof may not have been done before (or perhaps were done, but buried within a paper on a different topic or not even mentioned), i.e., there is something "new" here, but these aspects are barely incremental and do not qualify as significant advances. I also acknowledge that it can be incredibly frustrating for students and PIs because such characterizations are essential to being able to do new science or to understand a new instrument, but by themselves, the results are not broadly useful enough to justify further taxing the pool of over-taxed reviewers. Indeed the authors state this in a way, on page 11375: "Finally, even the smallest changes of the inner geometry of the instrument, e.g. caused by shipping, can affect ion beam alignment and thus cause different transmission characteristics."

It was exactly our goal not to burry our new method in another paper, but to make it available to other CIMS users in a clearly visible and consistent way.
The first advancement in our manuscript is the application of the established depletion method to a nitrate based CI-APi-TOF, which needs e.g. dedicated compounds to measure. The second advancement is the statistical analysis of the data which was necessary due to the clustering of compounds inside the instrument. This was so far not described and enables transmission estimation even with a spread of signal over a wide m/z region during depletion measurements.

That the ion transmission efficiency depends upon optics in the mass spectrometer is well known (as the authors describe), and it is even well known that electric fields in the ionization region affect mass transmission. For example, the PTR community and others have used this fact to ensure either that clusters are broken apart in the ionization region, and therefore have a very low transmission efficiency, or alternatively, are preserved and transmitted (e.g. Iodide and nitrate clusters). The stability of cluster ions, or lack thereof, in electric fields will by definition impart a real or apparent mass dependent effect on ion transmission in a way that depends not just on the ion mass but also composition. If different operators of the same type of instrument choose different electric fields (or pressures, etc) either intentionally or not, the effect will be different and thus 1 mass transmission curve is not relevant to data from a different instrument or even the same instrument with different voltage or pressure settings.

We fully agree on that and this is the reason why we submitted our description of the new method for obtaining these transmission curves to AMTD. We state in the manuscript, that our results should not be used for other instruments, but the method itself should be applied by other instrument users to improve the accuracy of ELVOC quantification.
As we list the flows and voltage settings as well as the chemical compounds, it is also possible for other CI-APi-TOF users to study the transmission efficiency with exactly the same settings and to compare with our derived transmission curves. This would be highly useful to understand the extent of instrument-to-instrument variability, and in how far these transmission efficiencies can be generalized if the exact same settings and compounds are used.

Explaining new insights into the fundamentals of what controls mass dependent ion transmission for a given system, or how to generally optimize those to arrive at a desired mass dependent transmission curve would both be a useful contribution, but the current paper does not offer that type of analysis.

We agree on that as well, but this is unfortunately beyond the scope of the present study.

The methods used for determining the transmission efficiency are not novel either. As part of ion molecule reaction rate constant determinations, Huey et al J. Phys Chem 1995 vol 99 No. 14 report doing exactly the same method of reagent ion titration as used in this manuscript to constrain the mass dependent ion transmission of a quadrupole mass filter. That paper is not referenced here.

They state "The mass discrimination was determined by measuring the ratio of the change in the product ion signal to the change in the reactant ion signal for several ion molecule reactions that produce only one product ion...."

We thank the referee for this reference and will include it in the revised manuscript, as it describes the depletion method as well for SF_6^- primary ions. The referee states that “exactly the same method” was used in this reference as in our manuscript. However, the given quote from Huey et al. explicitly says that the depletion method was used “for several ion molecule reactions that produce only one product ion.” The formation of only one product ion signal enables a simple fit, but for the CI-APi-TOF we don’t have this situation, as we have intense clustering of all compounds and thus a shift of charge not to only one, but at least two separate m/z regions. The clustering of compounds can be treated with the regression analysis introduced by our manuscript. This is clearly a new feature and not present (as fortunately not needed) in the study of Huey et al. and the applications of the depletion method in the PTR-community.

Junninen et al AMT 2010 use a DMA and electrospray ion source to constrain the mass dependent ion transmission of a Tofwerk APi-ToF.

We cite this paper in our manuscript and compare the method described there with our improved depletion method. Our conclusion was that the ion source itself has a clear effect on transmission efficiency. This is not that surprising (we agree with the referee here), but now we have a way of measuring it.

Thus, while I have zero criticisms of the methodology, data quality, or conclusions, I think this information is not sufficient for a stand alone paper, and would be better incorporated as part of another paper, or supplemental information for another paper that can always be referred back to by the authors when needed to support the fact that they do these determinations.

We are happy to see that the referee approves our methodology, data quality and conclusions. Concerning the question of importance, we argue (as mentioned already above) that the first detailed description of our easy-to-use method for obtaining transmission curves of a nitrate based CI-APi-TOF is an important improvement for ELVOC quantification. We recommend to other users to redo these measurements for their instruments and therefore argue in favor of a clearly visible and easily accessible stand-alone publication. Our findings are important for making results of different instruments comparable; and to achieve a more quantitative measurement of many compounds, such as ELVOCs for which a separate calibration is not feasible. Secondly, we have improved the long-known method of depleting primary ions by adding a special statistical analysis of the measured signal. This enables us to treat clustering of the introduced compounds, which was not the case (and not needed) in earlier applications of this method, but is crucial for the nitrate based CI-APi-TOF.
Last but not least we think that it is the idea of the journal “Atmospheric Measurement Technologies” to publish papers that focus on the methods and measurement technologies, i.e. papers that do not present “science”, but rather the underlying methodological and technological aspects that are a prerequisite for doing the science. For the reasons stated in our replies above, we think that the methodological advances are clearly substantial enough to merit publication in AMT. We also clearly favor to split up papers into a (not very long) method paper for AMT and a scientific paper in which the method is then just referenced, which makes the scientific paper shorter and therefore reduces the burden on the individual over-taxed reviewer.

References:

Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., Kostiainen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M., and Worsnop, D. R.: A high-resolution mass spectrometer to measure atmospheric ion composition. Atmospheric Measurement Techniques, 3(4), 1039-1053, 2010.

Huey, L. G., David R. H., and Carleton J. H.: Reactions of SF_6^- and I^- with atmospheric trace gases. The Journal of Physical Chemistry, 99.14, 5001-5008, 1995.