

Interactive comment on “Aerosol mass spectrometry: particle–vaporizer interactions and their consequences for the measurements” by F. Drewnick et al.

P. Herckes (Editor)

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For completeness of the discussion, I am posting here the follow-up exchange between a reviewer and the authors as an editor comment. Author replies are marked with "R:"

I thank the reviewers for considering my comments. I feel that the manuscript is very much improved, however there are a few things I still find myself at odds with and because of the very technical nature of the paper, I feel that these require further consideration before publication.

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R: We thank the reviewer for reviewing our revisions in great detail again. We further revised the manuscript along the comments in this review to a large degree.

I feel that the authors may have misunderstood my hypothetical mechanism for NH_4NO_3 vaporisation that produces a long decay time for NO^+ . Normally, NH_4^+ present in the particle phase vaporises as NH_3 , donating a proton to the NO_3^- to produce volatile HNO_3 in the process. However, if the proton produced during NH_3 vaporisation went elsewhere, being taken up by a yet-to-be-identified acceptor or released as a free hydrogen ion, then this would leave an excess NO_3^- ion on the surface of the heater. We know from the work with metal nitrates that nitrate volatilisation without HNO_3 production is slower and produces more NO^+ relative to NO_2^+ during ionisation, so could this be a reason for the observation?

R: We got the point of the reviewer. However, with the information which is available to us, and not knowing any details about the experiments the reviewer is referring to, it is hard to even discuss this potential process. In our experiments we observe a longer vaporization event length for m/z 30 compared to the other m/z . Applying the proposed explanation, this could only occur if this slow vaporization occurs for at least a large fraction of all nitrate molecules. This would mean that a large fraction of the protons donated by the NH_4^+ would not reach the NO_3^- even though they are likely close together at the beginning of the process and even though electrostatic forces should support the recombination of H^+ and NO_3^- . This is hard to imagine. Furthermore, this process needs a speculative acceptor for the proton or includes the emission of protons for which we also do not have any evidence. Finally, this process would leave negative NO_3^- ions which would either need two EI ionization steps or alternatively we would need another process to remove the charge from the NO_3^- ions on the vaporizer. All this might be possible. However, we do not have any evidence or reference for any of the several steps needed and could only speculate that they occur. Since we think that the proposed potential explanations are already sufficient to explain the observed behavior we do not think it makes sense to add another, highly speculative process.

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I'm not sure I follow the arguments for NO and SO_x being persistent on the basis of them 'surviving longer' and being at the end of their respective reaction chains. Once the vapours have left the immediate plume of a vaporisation event, then all further reactions should cease because the pressure will be too low. I would consider it far more plausible if the nitric and sulphuric acid were simply being removed from the system on the first collision with a surface due to their stickiness, whereas the lower oxides would be free to persist.

R: We agree that this effect – of efficient sticking of nitric and sulfuric acid molecules to the ionizer walls – will have an influence on observed vaporization event lengths for the associated signals. However, this would not explain the shorter vaporization event length of m/z 46, which is also from NO₂ and for which we would not expect that sticking to the ionizer walls would completely remove these molecules from the system. Therefore, we included this effect into the discussion as an additional possibility and changed the text accordingly: "Very sticky molecules like nitric acid and potentially NO₂ are likely removed from the system on the first collision with a cooler surface, prohibiting any extension of their residence time in the ionizer volume by adsorption/desorption processes. If these surfaces have a sufficiently high temperature thermal decomposition of these molecules with subsequent desorption of decomposition products might occur.", and further below in the text: "An alternative explanation for the longer duration of the vaporization event lengths for m/z 64 and m/z 48 signals compared to those of the other ions could be removal of H₂SO₄ from the system by condensation on cooler ionizer walls followed by slow thermal decomposition and vaporization of the decomposition products instead of re-desorption of the sticky H₂SO₄ molecules."

In spite of the revision to the section dealing with peak ratios relative to pulser frequency, I still find myself at odds with the authors on this issue. While it is conceptually possible that this could become an issue if single ions are missed because of ADC thresholding, this shouldn't happen if the instrument has been set up correctly. As

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part of normal operation, the user is supposed to verify that the single ion signals (e.g. m/z=40) are proportional to the multiple ion signals (e.g. m/z=28). If this is not the case, then the issue the authors describe would only be one of a number of problems with quantification, so the instrument should never be run in this state anyway. It should also be noted that the initial degradation in linearity (manifested by the 40/28 ratio) when thresholds are marginally too high is due to signal being lost from the 'tails' of the ion pulses, rather than entire ions being missed. In order to miss entire ions, an instrument would have to be in an extremely compromised state in this regard. This can happen through either user error or faults such as a preamplifier failure, but in those circumstances the data are regarded as unreliable anyway. While I can see how this phenomenon could conceptually be an issue for BFSP triggering (although the authors present no documentary evidence of this actually occurring), this mode of operation is generally only used during calibrations anyway, where the particles being used are large enough for this not to be an issue. To reiterate my original point (which the other reviewer seems to concur with me on), I do not see how this can affect the peak ratios in the modes of operation used for experimental work, specifically MS, PTOF, LS or FMS. While I would agree in advocating using a high pulser frequency for the sake of signal-to-noise ratio and PTOF resolution, I regard the problem that the authors describe as a complete non-issue, so I would question why it needs mentioning at all.

R: We absolutely agree with the reviewer that in regular averaged AMS measurements this effect should not occur since the ADC threshold is supposed to be set sufficiently low to allow the measurement of individual ions with high efficiency. If this is not the case there is an issue with the settings of the instrument and there are many other problems for the quantification as the reviewer stated. However, in BFSP single particle measurements using a signal threshold (when no light scattering module is available) and where the threshold for single particle detection is typically larger than the ADC threshold this can become a problem. In this case particles exceed the m46 threshold less often than the m30 threshold when only the tail of the particle vaporization event is measured – as also stated by the reviewer and reflected in Figure 2b where the lower

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end of the distribution for m/z 46 is cut off at low pulser frequency. In the manuscript we already have limited the statements on single particle measurements. To make this clearer we revised the text further: "This effect – of longer single particle vaporization event length of the m/z 30 ion (46 μ s full width half maximum, FWHM) compared to the m/z 46 ion (29 μ s) – can become relevant if the sampling frequency of the ions (i.e. the pulser frequency of the ToF-MS) is small and consequently the pulser period (i.e. the inverse of the pulser frequency) is in the order of the particle vaporization event length. With event lengths in the order of 25 to 40 μ s FWHM for many of the ions, this is the case for measurements with the HR-ToF-AMS (typical pulser periods: 20-40 μ s). As a consequence of the less frequent sampling of the ions into the MS not only a larger fraction of the ions is missed (i.e. the measured number of ions per particle (IPP) is reduced, Fig. 2b), but also the chance to measure only the very small signals in the tails of the vaporization events increases. Since this occurs more frequently for the shorter m/z 46 peak compared to the longer m/z 30 peak there is a larger chance for m/z 46 not to exceed data acquisition thresholds if they are not set sufficiently low for (e.g. in BFSP single particle measurements, Fig. 2b). This could result in a change in the fragmentation pattern of ammonium nitrate (m/z 30 to m/z 46 ratio) for these single particle data when the pulser frequency changes, while it should not affect regular averaged AMS measurements. Therefore – and due to the IPP changes – measurements should always be performed with a pulser frequency as high as possible (limited by the desired m/z-range of the mass spectra) and at the same pulser frequency as was used during calibration measurements."

Regarding table 1, while I can appreciate the need for minimising clutter, I would still prefer it if the actual numbers guiding the classification could be presented, perhaps as supplementary material. This would provide an element of objectivity to how the authors have classified the elements, otherwise it just comes across as obtuse and arbitrary.

R: At the end any classification of substances into "well" and "not so well" measurable is

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arbitrary. The purpose of Table 1 is to show that there are many inorganic substances which can be expected to be measurable with some efficiency with the AMS and which are not within the few standard AMS species, measured and identified on a regular basis. We think that by adding clear melting and boiling point limits for the classification into group I and II we already supplied the classification criteria. Of course – and already stated in the text – these limits are arbitrarily chosen. This would not change if we add all the individual melting and boiling point data to the table. However, adding this information would increase the size of the table by a factor of 4-5 which we do not see as adequate for the value of the added information. Furthermore, all these data can easily be found in a single on-line reference (Haynes et al. 2015, internet version). As a compromise we added the link to this reference and the chapter where this information can be found to the manuscript and leave the table as it is. This keeps the table legible and at the same time allows easy access to the information. If the editor wishes that we add all this information to the Table, we will add it.

Regarding the response to my query on P3539, L3, if the authors cannot provide any specific evidence for the increase in temperature improving the recovery rate, the observation should be presented as anecdotal.

R: We reworded the text according to the reviewer's comment: "For iodine the sticking efficiency is so large that even weeks after such a measurement significant background signal levels are observed (Drewnick et al. 2009). We observed slightly faster decay of this background signal when heating the vaporizer to an elevated temperature for several days."

Regarding the issue of bounce raised by the other reviewer, I am aware of (possibly unpublished) results within the AMS users community based on LS mode data that would indicate that bounced particles may still vaporise, so the authors should perhaps not be so quick to discount this as a possibility.

R: The reviewer is right. In measurements with an AMS equipped with a light scattering

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probe delayed particle vaporization events have been observed which were explained with vaporization of particles which first bounced off the vaporizer and which vaporized when they hit the vaporizer a second time (it is inverted cone shaped) or when hitting hot ionizer surfaces. We did not operate a light scattering probe in our experiments and therefore had no possibility of observing such delayed vaporization events. Therefore we cannot provide any information about potential vaporization of bounced particles. We included this information in the text: "Bounced particles are generally assumed to be lost for the analysis and accounted for by applying a collection efficiency correction factor (CE, Canagaratna et al., 2007). Using an AMS equipped with light scattering module delayed particle vaporization events have been observed which were explained by bounce of particles off the vaporizer and delayed vaporization upon secondary impacts with the vaporizer edges or hot surfaces of the ionizer (Cross et al. 2009). Since we did not find any evidence for vaporization of bounced particles in our experiments we do not further discuss this possibility here."

I find myself at odds with the other reviewer regarding point 40. At STP, mercury is a liquid and as such, it is reasonable to include in this table. While it also exists as a vapour in thermodynamic equilibrium with the condensed phase, it is still far below its boiling point.

R: We included mercury again in Table 1.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 3525, 2015.