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

**Anonymous Referee #1**

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This paper is important and covers fundamentals issue regarding the functioning of the Aerodyne Aerosol Mass Spectrometer. While the issues described do not affect instrument performance during most atmospheric applications, they may be important in certain environments, during direct sampling of sources or laboratory studies. It may also shed light on some of the less well understood phenomena encountered during routine work, such as the formation of fragments from semi-refractory organic matter. This work is very relevant to AMT and deserves to be published, but I have a number of comments that I would like to see considered first. I should stress however that most of these comments regard the presentation of the fundamental science and

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general organisation of the results; because the results and implications are dealt with empirically, these issues should not impact the practical findings of the paper.

General comments:

My single biggest general comment would be that most of the detail with this paper is handled in a very qualitative way without much attention to quantitative data, verifiable processes or hard-and-fast recommendations. For example, results such as recovery times are handled in an inconsistent manner and there are many instances where data is referred to but not presented. As a constructive criticism, I would say that these inconsistencies and omissions significantly weaken the general quality of the paper. There are also some areas where the authors present explanations and mechanisms that I find tenuous or counterintuitive. It may very well be that these are correct and I invite the authors to educate me on these, but currently, they are presented in a very qualitative and unsubstantiated way, so I do not find them particularly convincing. To strengthen their arguments, the authors should ideally include more references and/or quantitative calculations to back their assertions up. More specific areas for improvement are given below.

The authors are very ambiguous when it comes to the fundamental processes that govern the vaporisation and this results in some confusing and sometimes inaccurate definitions. 'Vaporisation' is a process that can occur at any temperature (for example, liquid water can vaporise at room temperature), so there is no such thing as a 'vaporisation temperature' as a fundamental property of a substance. Rather, there will be a boiling or sublimation point, at which all the material should exist in the gas phase. There is also a failure to distinguish between equilibrium thermodynamic properties and the kinetics of vaporisation. While the two are related (both being governed by molecular weight and intermolecular forces), one property does not explicitly dictate the other and vice versa. For instance, it is not clear how the authors relate the melting point to the vaporisation kinetics and I have pointed out other inconsistencies in the specific comments.

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The chemical reactions R1-R6 all require clarification. I find a number of aspects of them very counterintuitive and because they are not referenced, I feel I must question them. Firstly, I am not sure that they can all be described as reversible reactions; R1 in particular would always favour the separation of HNO<sub>3</sub> and NH<sub>3</sub> at the low pressures experienced here and the reversal of R2 should not be possible without some intermediate step because NO<sub>2</sub> is generally inert to both H<sub>2</sub>O and O<sub>2</sub> and the implied reaction would require an NO<sub>2</sub> molecule to simultaneously collide with both an H<sub>2</sub>O and an O<sub>2</sub> molecule. Moreover, because fragmentation occurs in the absence of nonparticipating gas molecules (e.g. N<sub>2</sub>) that would otherwise be available to quench the excess energy produced during recombination, if the products of any thermal fragmentation were to recombine in the vapour plume, I would naively expect them to immediately re-fragment. Finally, I find the 1/2O<sub>2</sub> notation in R3 and R6 to be needlessly ambiguous; the authors should specify whether it is oxygen atoms being produced, or whether two fragmenting molecules need to combine to produce a single O<sub>2</sub>.

I find the explanation that the NO and SO<sub>x</sub> signals' longer decay time is due to persistence in the ionisation region both speculative and counterintuitive. Firstly, I would not expect NO<sub>x</sub> and SO<sub>x</sub> to interact more with the ioniser surfaces, given that HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> are generally considered to be much 'stickier' molecules (unless the authors are arguing that the acids permanently stick to the surfaces in the event of a collision, in which case they should specify this). Secondly, there is another possible explanation for the longer decays in that if a portion of the NH<sub>4</sub><sup>+</sup> can vaporise without returning a proton to the corresponding anion (through a yet-to-be-identified mechanism), then stoichiometrically, a corresponding portion of the nitrate and sulphate will not be able to vaporise as HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>. As such, they may vaporise in other forms, processes which will take longer, as demonstrated by the slow vaporisation of metal nitrates. If this cannot be discounted, it should be added as a possibility.

When the authors refer to the decay of signals in the instrument (e.g. page 3538), it would be very useful if they could discuss these decays in terms of exponential decay

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coefficients. If they do not decay exponentially, then they could still generate general statistic such as the half-life. This added consistency would allow the behaviour of the different molecules to be compared much more directly and easily.

The statement that the possible non-detection of vaporisation in certain channels will cause the fragmentation pattern to change should not be true for the normal MS and PTOF modes of operation (as currently implied); while some fraction of the  $m/z$  46 events will be missed due to the short vaporisation times, the relatively high instantaneous intensity of these events means that the as the collective signal from a large number of detected events is accumulated, the average signal will still be a quantitative reflection of the total amount of material available for detection. As such, the 30/46 ratio will be preserved, regardless of the pulser frequency. I should note that I can see how it can introduce a bias in the BFSP ratio (as implied but not quantified in figure 2) due to the requirement that sufficient signal is needed to trigger data collection. If the authors wish to prove it causes an effect (which would be a very significant result), it is a very simple experiment to perform, where the 30/46 ratio (in all three modes) is reported as a function of pulser frequency on the CTOF.

Specific comments:

P3527, L3: A definition for 'flash vaporisation' should be provided, to distinguish it from any other forms of vaporisation.

P3532, L24: The longer vaporisation time needs to be more explicitly linked to the higher 'vaporisation temperature'. Is the implication that the kinetics of the vaporisation process (once sufficient energy is attained) are slower, or it takes longer to conduct the necessary heat from the vaporiser to the molecules?

P3535, L20: Asides the issues mentioned in the general comments, thermal decomposition into more volatile components (e.g.  $\text{NO}_2$ ) may occur before vaporisation as  $\text{KNO}_3$ , so the bulk properties of the salt may not be valid here.

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P3537, L11: The authors should specify what they mean by 'not far'. The authors should explain if there is a physical basis for expecting the vaporisation kinetics to be governed by the melting point, or whether this is merely a convenient proxy that empirically seems to work (as implied later in the manuscript).

P3537: A number of decomposition temperatures are referred to, but it's not clear where they are coming from or what mechanisms they refer to. Are these also from Haynes et al.? Actually listing the melting/decomposition point data in table 1 (with references where appropriate) would be informative, along with the corresponding data for the species not considered detectable so that a good comparison can be made.

P3539, L3: Some quantitative data to back this up would be good.

P3542, L28: While matrix effects with ammonium are well known, have these been observed with other cations?

P3546, L4: Related to the general comment about the vaporisation of nitrate, an alternative reason for the effect of water being present could relate to the fact that liquid water helps to facilitate proton transfer (this is a staple of acid-base chemistry), so this could ensure that more of the nitrate vaporises in the form of HNO<sub>3</sub> rather than NO or NO<sub>2</sub>.

P3546: The correlation between the 80, 81 and 98 signals and the water background is interesting, but I find the explanation hard to swallow; while the concentration of gas molecules within the immediate vapour plume may be sufficient for further interactions after leaving the condensed phase, the pressure of background gases is such that the mean free path will be on the order of kilometres, so significant direct interactions in the gas phase would seem unlikely. The authors are welcome to prove me wrong on this point, but I would need to see some hard maths to be convinced. While one speculative explanation could be that the interactions are occurring on the vaporiser or ioniser surfaces (which background water molecules will attach to), the authors should verify that the correlation observed was not the result of a common cause as opposed

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to direct causation; they currently do not specify what was causing the water vapour background to vary or even how much it was varying by, so without knowing these details, it is difficult to say with certainty that this was in turn causing the changes in the sulphate fragmentation pattern. A much more thorough explanation is warranted.

P3547, L17: To be clear, is it the authors' opinion that WO<sub>3</sub> is routinely formed but remains in the solid phase on the vaporiser surface, then is subsequently liberated as WO<sub>2</sub>Cl<sub>3</sub> when it reacts with chloride? The subsequent text seems to be consistent with this, but the authors should be specific about this here because currently, it may imply that WO<sub>3</sub> is continuously produced in the gas phase under normal running conditions, which is not the case.

P3548, L18: It would be useful to give actual numbers for the yields rather than the rankings, e.g. in the form of a table.

P3549: It should be mentioned that the efficiency of the K<sup>+</sup> surface ionisation is also affected by the setting of the heater bias voltage. The authors should also verify that this was not changed during the experiments presented here.

P3550: It is worth mentioning here that the two-stage detection of KCl is analogous to the detection of NaCl documented by Ovadnevaite et al., as the latter is an established observation.

P3550: I'm not sure how the statement "Measurements at this vaporizer temperature have shown that apparently a large fraction of the ions generated by surface ionization get lost on their way to the mass spectrometer when the filament is on" is supported by the data. The authors should either back this up with numbers or generally explain it better. But besides this, the physical explanation offered (at least, how I interpreted it) is not plausible because the state of the filament does not affect the voltages inside the ioniser cage, which are dictated by the ioniser, heater bias and extraction voltages. In my opinion, a more likely explanation would be the presence of the electrons mitigating the mutual repulsion of the high spatial density of potassium ions. Or perhaps the

hot filament is changing the performance of the vaporiser surface through radiative heating. A possible means of separating these effects would be to set the filament voltage to the ioniser voltage rather than switching the filament current off (assuming that this doesn't swamp the ioniser with surface ions from the filament). As regards the comparison to the electron ionisation, could it also be possible that if a significant fraction of the available potassium is surface ionised, the neutral vapour available for electron ionisation becomes depleted?

Technical comments

P3527, L2: Rephrase “is used since decades” to “has been used for decades”

R1, R4: The use of the ‘up arrows’ is not appropriate here; this is generally used in wet chemistry to denote a reaction product transferring irreversibly to the gas phase, whereas these reactions are being presented as taking place on the surface of the vaporiser or in the vapour plume.

P3532, L22: Insert a comma after “sulfate”

Figure 5: For the sake of good practice, the x axes on these graphs should start at zero.

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

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