Atmos. Meas. Tech. Discuss., 8, C2071–C2129, 2015
www.atmos-meas-tech-discuss.net/8/C2071/2015/

Atmospheric
Measurement
Techniques
Discussions

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

F. Drewnick et al.

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Received and published: 18 July 2015

R: We thank the two anonymous reviewers for reading our manuscript very thoroughly and providing many helpful comments. We agree completely with most of the comments of the reviewers and implemented them in the manuscript. We are convinced that this improved the manuscript and strengthened it a lot.

Anonymous Referee #1

Received and published: 20 May 2015

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 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.

R: We tried to generally strengthen the paper with regard to quantitative information and clear recommendations. As specified in the detailed comments and replies below we changed the text at several locations in this regard, e.g.: - We added the values for the yields of WO2Cl2 generation for all substances which were tested. We also added quantitative information on the fractional contribution of the WO2Cl2-related signals to the mass spectra. For this purpose we added another table to the manuscript. - Instead of a single vague statement about which substances might be measurable with the AMS we introduced two groups of substances with clearly defined melting and boiling point limits and defined for each substance to which group it belongs. - We thought about how to present recovery times in a both consistent and adequate manner already before we wrote the first version of the manuscript. As detailed below exponential decay parameters or half-live values do not make sense due to the specific conditions observed. Therefore we consistently provided the fractional decay after a certain time after (10s) the change of the measurement conditions. We think this is the most appropriate way to present the results in a consistent way - We discussed the data on matrix effects in a separate paragraph which have been mentioned only previously but not presented. - We added a panel in one of the figures showing data which have so far only been mentioned but not shown. In addition we added several clear statements and recommendations to the conclusion section of the manuscript to provide directly useable information to the AMS user.

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.

R: The reviewer is absolutely correct. The term “vaporization” was several times used synonymous with “boiling” which is not correct. We re-worded all these passages to comply with the definition of “vaporization”. Regarding the qualitative presentation of arguments, we also revised the text at many locations in order to improve this. For more information, please see the replies to the specific comments below.

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.

R: It is not our intention to equate equilibrium thermodynamic properties with kinetics of vaporization. In order to distinguish more clearly between them we re-worded the text at several locations. E.g. the term “vaporization” was more clearly used according to its definition (see comment above); furthermore, it was stated more clearly that the melting point is only used as an empirical proxy which can be used to decide whether a substance can be expected to be measurable with the AMS or not and is not physically related to the vaporization kinetics.

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 HNO3 and NH3 at the low pressures experienced here and the reversal of R2 should not be possible without some intermediate step because NO2 is generally inert to both H2O and O2 and the implied reaction would require an NO2 molecule to simultaneously collide with both an H2O and an O2 molecule. Moreover, because fragmentation occurs in the absence of nonparticipating gas molecules (e.g. N2) 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 refragment.

R: We think that Reaction R1 and R4-R6 are equilibrium reactions under conditions where sufficient interaction between the molecules is possible. This is likely the case during the very early phase of the vaporization process, when the material is in transition from a solid or liquid to a vapor. Very quickly, when the vapor plume expands into vacuum the reactions will be more and more kinetically limited. Therefore, we agree that writing them as irreversible reactions reflects better what actually happens in the complete vaporization process. We therefore changed this according to the reviewer's suggestion and revised the description of this below the equations: "While in the very early phase of the particle vaporization when the vapor density is still high, reaction R1 as well as the reactions presented further below (R4-R6) can be assumed to be equilibrium reactions, under the conditions in the AMS they will be very quickly kinetically limited due to the expansion of the evolving vapor from the vaporizer into the surrounding vacuum." In addition, we added references for the reactions.

Finally, I find the 1/2O2 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 O2.

R: R3 and R6 have been changed to clarify this. Both sides have been multiplied by 2.

I find the explanation that the NO and SOx signals' longer decay time is due to persistence in the ionisation region both speculative and counterintuitive. Firstly, I would not expect NOx and SOx to interact more with the ioniser surfaces, given that HNO3 and H2SO4 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 NH4+ 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 HNO3 or H2SO4. 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.

R: We agree that HNO3 and H2SO4 are much "stickier" molecules compared to NOx and SOx. The idea behind the explanation for the longer evaporation event length of

NO compared to the other molecules is that these molecules survive the decomposition process longest (they are the end-products) and therefore have a chance to adsorb/desorb from the ionizer walls causing a longer effective vaporization event length. We re-worded the respective text to make this clearer: "A possible explanation for the longer appearance of the m/z 30 signal – after the other signals already have decayed (Fig.2a) –is that the NO molecules, as end products of Reactions (R1) to (R3), survive the high temperature condition longest. Therefore they have the potential to stay longest in the ionizer volume, likely further extended by adsorption/desorption to the ionizer walls." We find the suggested additional mechanism of "non-equilibrium vaporization" rather speculative. We do not have a good explanation for such an effect of vaporization of NH4 molecules and also no reason to assume that the material that would remain after this would vaporize slower. Furthermore, we do not observe any NH4+ ions in the mass spectra, which we would expect if this process would occur. Since our proposed mechanism seems rather intuitive to us we did not add this additional process. However, to make clear that our suggestion is just a possible explanation we wrote this in the text as shown above.

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 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.

R: The decay behavior of signals in the AMS is a consequence of the underlying processes that cause the vapor concentration in the ion source to decay over time. For a certain vapor molecule in an ion source of homogeneous temperature, this would likely be an exponential decay – e.g. when only looking at the decay of molecules vaporizing of the AMS vaporizer. However, as already described in this manuscript and in more detail in (Drewnick et al., 2009), as a consequence of surfaces at very different temperatures surrounding the AMS ion source, the decay of the vapor background in the instrument slows down as decay time progresses since vapor molecules originate more and more from cooler surfaces. Therefore description of the decay with a single or a small number of exponential decay coefficients is not possible and would not properly reflect the situation in the ion source. Also the use of half-life values is not very helpful since they would also not properly describe the situation in the ion source; in addition, several of the molecules do not even decay to half their initial value during the measurement time, so for some measurements these values could not be provided. We completely agree with the reviewer that we need a consistent way to describe the decay process to allow comparisons. Therefore we thought about this issue before and came to the conclusion that the best way to present the decay behavior in a consistent way which allows comparison between the different molecules is to present the decrease within the first 10 seconds (this is two measurement cycle lengths, this was chosen because for one cycle length one would have a relatively large uncertainty of the exact time within this cycle when the measurement was performed – i.e. the 1 s measurement out of the 5 s cycle in relation to the exact time of switching the aerosol) and the decrease until the end of the decay time measurement. We did this consistently over the manuscript. Since we think this is the most useful way of presenting this information in a consistent way we do not change this approach to a different one which would probably not cover the whole range of observations.

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.

R: The reviewer is completely right: as long as all signals are actually collected by the instrument for measurements where many single particle vaporization events are averaged (i.e. MS and PTOF mode measurements) the average signal intensity for both m/z will correctly reflect the particle vaporization event area since sampling will be evenly distributed over the particle vaporization event. However, as also indicated by the reviewer, as soon as there is a chance for small signals not to exceed a data acquisition threshold and being rejected for detection, a general decrease in signal intensity can result in a stronger decrease in detected signal intensity for smaller signals compared to larger signals. As a consequence the signal ratio (i.e. the fragmentation pattern) can change. This effect can occur in single particle measurements where only particles exceeding a certain signal threshold are detected or in averaged measurements (MS or PTOF) when the data acquisition threshold is high enough that some of the single ion signals are missed. Since this effect is rather a question of threshold settings and not of vaporization event lengths, we only briefly mention it and do not discuss this further. In order to make the situation clearer we re-worded the respective text partially: “This effect – of longer single particle vaporization event length of the m/z 30 ion (46 μs full width half maximum, FWHM) compared to the m/z 46 ion (29 μs) – 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 μs FWHM for many of the ions, this is the case for measurements with the HR-ToF-AMS (typical pulser periods: 20-40 μs). 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 very often very small signals (i.e. individual ions) 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 individual ions (e.g. in 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) when the pulser frequency changes. 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."

Specific comments:

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

R: There is no single rigid definition for "flash vaporization", a term which is used for different applications in science and engineering. Therefore we added an explanation for this term for the application referenced here: "Flash vaporization, i.e. very rapid vaporization (here in the order of a few tens of microseconds) of a sample by contact with a hot surface, in combination with mass spectrometry has been used since decades for the analysis of thermally fragile (e.g. Lincoln 1965, Chinn and Lagow 1984) or environmental (e.g. Leeuw et al. 1986) samples with little or no pre-treatment needed."

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 vaporization process (once sufficient energy is attained) are slower, or it takes longer to conduct the necessary heat from the vaporiser to the molecules?

R: We think that both effects might impact the length of the vaporization events. The higher "vaporization temperature" means that more heat needs to be conducted into the particle before quick vaporization and in addition the kinetics of the vaporization process itself might be slower. We changed the text accordingly to: "For ammonium sulfate generally slightly longer particle vaporization events are observed, compared to ammonium nitrate (Fig. 2c), both for the sulfate-related ions but also for those associated with ammonium. This difference can possibly be explained by the higher temperature needed for quick vaporization of $(NH_4)_2SO_4$ compared to NH_4NO_3, which might result in more time needed to conduct the necessary heat into the particles and potentially slower vaporization kinetics."

P3535, L20: Asides the issues mentioned in the general comments, thermal decomposition into more volatile components (e.g. NO_2) may occur before vaporisation as KNO_3, so the bulk properties of the salt may not be valid here.

R: The wording in the text was unfortunate. As stated by the reviewer there is a good chance that KNO_3 thermally decomposes before vaporization. According to CRC Handbook of Chemistry and Physics KNO_3 melts at 337 °C and thermally decomposes at 400 °C. On the other hand, NH_4NO_3 thermally decomposes at 210 °C. To account for all this we reworded the sentence: "Since quick vaporization of KNO_3 occurs at higher temperatures compared to NH_4NO_3 the thermal decomposition, albeit partially along different chemical pathways, progresses further for this species before ionization."

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).

R: The use of the melting point as an indicator whether a substance might be measurable with the AMS or not is rather a convenient proxy than strictly based on physical principles. The physical principle behind this idea is that substances which are more strongly bound will vaporize less efficiently at a certain temperature and that vaporization under vacuum conditions will likely occur efficiently somewhere between the melting and the boiling point. To make this clearer and to set clear limits into which category individual species are sorted we introduced two "groups" of substances, defined according to their melting and boiling points or decomposition temperature and reworded the text: “From our experience, as an empirical proxy, a substance can typically be measured in the AMS with some efficiency if its melting point is not far (< 200°C) above the vaporizer temperature. From comparison of melting (MP) and boiling point (BP) as well as thermal decomposition data (Haynes et al. 2015) with the typical AMS vaporizer temperature (550-600 °C) one can identify substances that can be expected to be measurable with the AMS. We arbitrarily divided these substances into two groups of species which can be expected to be measureable quite well with the AMS (Group I; MP<600 °C and BP or decomposition temperature <900 °C) and which can be expected to vaporize rather slowly, but still sufficiently fast for detection with the AMS (Group II, MP<800 °C and BP or decomposition temperature >900 °C).”

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.

R: All melting, boiling, and decomposition temperatures were taken from Haynes et al. 2015. In the re-worded text (see last comment) this is stated more clearly. In order to keep Table 1 better legible, we did not add the temperatures to this table. However, we divided the individual species which can be expected to be measurable with the AMS into two groups, depending on their melting and boiling (or decomposition) temperatures (see reply to previous comment) and indicated the affiliation to these two groups in Table 1 by printing the symbols in bold (group 1) or normal (group 2) font.

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

R: Removal of contaminations in vacuum chambers by long pumping times and quicker removal by heating the chamber is a well-established procedure. We also observed that after heating the vaporizer to an elevated temperature and pumping for a day or a few days we can reduce background levels after contamination significantly –

similar to weeks of just pumping at normal temperatures. However, we never quantified how quick this cleaning occurs as a function of temperature. To do this would be an enormous effort with only little gain in information. Therefore we unfortunately cannot add this information here.

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

R: We have not observed such effects with other cations than ammonium. Since this sentence is a very general statement we did not want to exclude other possible sources of matrix effects. In order not to make statements beyond our measurements we remove “e.g.” from the text which reads now: “Finally, several experiments have provided evidence for matrix effects where as a consequence of chemical reactions of the semi-refractory aerosol component with a matrix component (ammonium) significant changes in vaporization kinetics (i.e. in c/o ratios) were observed, which in turn result in changes in RIE.”

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 HNO3 rather than NO or NO2.

R: After intensively discussing this issue with multiple persons we came up with the following reply: If we understand correctly, the reviewer suggests that NH4NO3 vaporizes as NH3 and HNO3 (as shown in R1) in the presence of water (as a consequence of proton transfer facilitated by water in the particles) and that it vaporizes as NH4 and NO3 (ions or radicals) under dry conditions. The latter process seems rather unlikely to us from our basic understanding of the processes. Furthermore, this would mean that under dry conditions we would need to observe NH4+ in the mass spectra. This is not the case. We always observe only NH3-related ions. Possible products from heating ammonium nitrate could be either the thermal decomposition products of ammonium nitrate (N_2O and H_2O) or NH_3 and HNO_3. Since N_2O is not observed in the mass spectra either we conclude that most likely NH_3 and HNO_3 are generated in the AMS when ammonium nitrate is vaporized on the vaporizer. Therefore we think that in the AMS ammonium nitrate always vaporizes as described in R1. This is the effect of proton transfer as described by the reviewer. We assume that R1 and R4-R6 are equilibrium reactions during the very early state of particle vaporization, when the vapor density is still high. As the expansion of the vapor into the plume progresses the vapor density reduces and these reactions become kinetically limited. In this kinetically limited transition phase there could be the possibility that more water in the particles quenches the thermal decomposition of HNO_3 into NO_2, H_2O and O_2 (R2), resulting in increased HNO_3-related signals. We therefore re-worded and extended the possible explanation for the shift in the nitrate fragmentation pattern: “The tendency of increased m/z 46 and 63 signals with increasing aerosol RH reflects that a larger fraction of the nitrate is measured as HNO_3 and possibly NO_2 instead of further decomposition products. A possible explanation could be quenching of the thermal decomposition of HNO_3 (R2) due to higher abundance of water, which could take up energy from the HNO_3 molecules during vaporization.”

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 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.

R: We agree with the reviewer that due to the very low density of background water vapor molecules it is virtually impossible that these molecules have a measurable interaction with the vapor molecules from the particles. We therefore re-worded this section and removed the explanation for the observed behavior. Since we do not have more than speculative explanations we do not provide any explanation for this observation. In addition we added information on the range of water background variation observed in the experiments. The text reads now: “For ammonium sulfate no significant changes of relative signal intensities (related to the intensity at m/z 64) were found when the aerosol RH was increased from 1.5% to 85%; for the various ions, average changes of relative signal intensities ranged from -4% up to +3% with an average uncertainty of ±19%. Only when correlating the relative signal intensity with the H_2O ionizer background signal (beam closed m/z 18, H_2O^+, related to the amount of water introduced into the instrument during recent measurements) a significant increase in m/z 80, 81, and 98 signal intensity with increasing water instrument background level was found. From linear regression of the data an increase of (+38±18) % was found for the m/z 80 signal, of (+27±16) % for m/z 81, and of (+28±17) % for m/z 98 over the range of water vapor background signal levels (303-322 kHz) measured within this experiment. These results suggest that also the efficiency of sulfuric acid decomposition is somehow related to the presence of water in the process, however, this dependence results in very small and typically negligible changes in fragmentation patterns.”

P3547, L17: To be clear, is it the authors’ opinion that WO_3 is routinely formed but remains in the solid phase on the vaporiser surface, then is subsequently liberated as WO_2Cl_3 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_3 is continuously produced in the gas phase under normal running conditions, which is not the case.

R: Our opinion about the formation of WO3 and WO2Cl2 is as indicated in the first part of this comment. To make this clearer in the manuscript we re-worded the respective text: “Apparently the WO2Cl2 in the vapor phase is a result of the reaction of Cl from the particles with the vaporizer surface, likely with WO3 that is generated by oxidation of the hot tungsten vaporizer surface by oxygen from the aerosol carrier gas (Wiberg, 2007) and accumulates on the vaporizer surface.”

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.

R: We added a table (Table 4), which contains the individual WO2Cl2 yields for the measurements of the various substances. In addition, this table also contains the relative contribution of the WO2Cl2-related signals to the mass spectra for each of the substances.

P3549: It should be mentioned that the efficiency of the K+ 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.

R: During the investigation of K+ ions from surface ionization we did not change the heater bias voltage. As suggested we added this information to the text: “Experiments to investigate the surface ionization process support the above-mentioned picture. Since the efficiency of K+ ions from surface ionization to be transported into the mass spectrometer strongly depends on the setting of the heater bias voltage, this setting was kept constant during these investigations.”

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.

R: We added this information and the reference to the text: “This shows that two different processes occur on the vaporizer: KCl partially vaporizes and in a second step this vapor is ionized by electron impact only; additionally, K atoms occurring at the vaporizer surface can undergo surface ionization with an efficiency depending on the temperature and the work function of the vaporizer, similar to what was observed for NaCl measured with the AMS (Ovadnevaite et al. 2012).”

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 asides 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?

R: During measurements at 800 °C vaporizer temperature we observed a potassium (39K+) signal of 16,400 μg/m^3 NO3-eq. during measurements with the filament on and of 49,800 μg/m^3 NO3-eq. (here the detector was saturated so the signal was even larger in reality) during measurements with the filament off. The difference of these two measurements (filament on minus filament off) is negative, so this cannot be the contribution of EI-generated ions. Since turning off the filament would not increase the temperature of the vaporizer this can also not be an effect of vaporizer temperature change. Therefore we conclude that the electrical field (not the voltages) in the ion source is changed when the filament is turned on. This change is apparently in a way that reduces the efficiency of K-ions from surface ionization to reach the mass spectrometer. This is likely an effect of the charge of the electrons introduced into the ionization volume as also suggested by the reviewer. To make this clearer we revised the text: “Measurements at this vaporizer temperature have shown that the K+ signal is more than three times larger when the filament is turned off compared to the situation with the filament turned on. This result suggests 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. This is likely due to associated changes of the electric field in the ionizer volume when the filament is turned on and off possibly as a consequence of the presence of electrons from the filament in the ionizer volume.”

Technical comments

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

R: done.

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.

R: The “up arrows” were removed.

P3532, L22: Insert a comma after “sulfate”

R: done

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

R: done

Anonymous Referee #2

Received and published: 4 June 2015

The paper by Drewnick et al. presents laboratory data for a number of particle types analyzed by several Aerodyne Aerosol Mass Spectrometers (AMS). These instruments are used by many groups, sometimes without fully appreciating the complexities of the detection process. The authors should be commended for conducting and documenting this interesting set of experiments that will serve as an excellent reference for AMS practitioners. The paper contains new data on AMS measurements of several semirefractory species and is of high interest for the audience of AMTD and generally well written. However in places it is not completely clear. I recommend that the paper is accepted into AMTD after the issues listed below are addressed.

Abstract

1) Line 6: suggest changing "various ambient aerosol components" to “various nonrefractory ambient aerosol components"

R: done.

2) Line 6-8: I assume that the authors are referring to the assignment of metal species to organic in the default analysis procedure when they say that results can be "misinterpreted". To my knowledge, this issue should only affect unit mass resolution analyses, and not high-resolution analyses. Moreover, since the metal species have unique ions and isotope patterns that do not resemble typical AMS organic spectra observed in ambient environments they can be readily distinguished and identified with additional analysis even in unit mass resolution. I suggest changing the last sentence to clarify this as follows: " However, when measuring close to certain anthropogenic and marine sources of semi-refractory aerosol particles, several of these assumptions may not be met and unit-mass resolution spectra should be carefully analyzed for unique ions and isotope patterns associated with semi-refractory species."

R: The reviewer is correct: when analyzing high-mass resolution data such signals from semi-refractory species can easily be identified. However, here we referred not only to the assignment of metal species to organics but also to potential incorrect quantification of signals as a consequence of slow vaporization. To make this clearer we re-worded the text: “However, when measuring close to certain anthropogenic or marine sources of semi-refractory aerosols, several of these assumptions may not be met and measurement results might easily be incorrectly interpreted if not carefully analyzed for unique ions, isotope patterns, and potential slow vaporization associated with semi-refractory species.”

3) Line 16: as discussed below, the differences in evaporation kinetics can lead to higher noise, but not to biases in ion ratios.

R: As long as all signals are actually collected by the instrument in measurements where many single particle vaporization events are averaged (i.e. MS and PTOF mode measurements) the average signal intensity for both m/z will correctly reflect the particle vaporization event area since sampling will be evenly distributed over the particle vaporization event. However, as soon as there is a chance for small signals not to exceed a data acquisition threshold and being rejected for detection, a general decrease in signal intensity can result in a stronger decrease in detected signal intensity for smaller signals compared to larger signals. As a consequence the signal ratio (i.e. the fragmentation pattern) can change. This effect can occur in single particle measurements where only particles exceeding a certain signal threshold are detected or in averaged measurements (MS or PTOF) when the data acquisition threshold is high enough that some of the single ion signals are missed. Since this effect is rather a question of threshold settings and not of vaporization event lengths, we only briefly mention it in the text and do not discuss this further. We revised the text here to make this clearer: “Even though non-refractory components (e.g. NH4NO3 or (NH4)2SO4) vaporize quickly, under certain conditions their differences in vaporization kinetics can result in undesired biases in ion collection efficiency in thresholded measurements.”

4) Line 26: clarify that the biases are due to semi-refractory species by changing the sentence as follows: " while laboratory experiments and measurements and measurements close to anthropogenic or marine sources of semi-refractory aerosol can be biased by these effects". A quantitative description of the magnitude of the effects studied would be useful.

R: We revised the text to make the influence of semi-refractory aerosols clear: “Laboratory experiments that investigate these particle–vaporizer interactions are presented and are discussed together with field results showing that measurements of typical continental or urban aerosols are not significantly affected while measurements of semi-refractory aerosol in the laboratory, close to anthropogenic sources or in marine environments can be biased by these effects.” Since these effects can have a very large variety and magnitude of influences on the data we did not include all this information in the abstract to keep the abstract shorter and more legible.

Introduction

5) p. 3528, Line 2: The assumptions are not “hard-coded”, they are user editable and users in fact are required to edit several entries for quantitative results with a specific instrument. Users are also strongly encouraged and responsible for adapting the frag table framework for their purposes and specific species studied, which the software interface makes easy to do. I suggest replacing with “hard-coded” with “user-editable,” and potentially explaining what the possibilities and responsibilities of users in a little more detail.

R: We completely agree with the reviewer’s comment. The word “hard-coded” is not adequate here. We revised the text accordingly and also added a short statement of the user’s responsibility: “For the standard analysis of the unit mass resolution spectra these associations are listed in the “frag table”, which needs to be adapted for special measurement situations by the user.”

6) p. 3528, Line 3: Huffman et al. (ACP 2009) also report the increase of the back-

ground (“closed”) concentrations as a fraction of the difference concentrations, for both ambient sampling and when sampling through a thermal denuder, for two different field studies. See Figures 4 & 8 on that paper.

R: We assume that this comment is associated to the text on p. 3528 line 24 and following. We added this reference to the text.

7) p. 3528, Line 28. The text “For less volatile or very “sticky” species” can be confusing, since it is not clear what the volatility of the species is, relative to non-refractory species. For example, sulfate is non-volatile from an atmospheric point of view, but is still non-refractory for AMS detection purposes. It would be better to say “For semirefractory species” which is clearer in the context of the AMS.

R: Changed according to the reviewer’s suggestion (we used the term “semi-refractory” to be consistent with the rest of the manuscript).

Measurement Setup

8) The time resolution at which the measurements were averaged and saved (in MS mode) should be described, since this may affect the interpretation of the fastest transitions observed (if the averaging time is longer than the timescale of the transition). Recent versions of the ToF-AMS acquisition software (since _2009 or so) allow acquiring data with time resolution of 1 second (Kimmel et al., 2011).

R: The various types of measurements presented in this manuscript have been performed with different AMS instrument settings, including different open/closed cycle lengths of the MS mode data. Therefore we prefer to describe the relevant settings of the instrument in the individual sections of the manuscript. The time resolution of the measurement is already presented in the results sections where appropriate. The measurements of section 3.2 have been performed before the new version of the data acquisition software was available. Therefore the best time resolution we could achieve was 5 seconds. This is already stated in the respective section.

9) The data analysis software used and any relevant adjustments and settings should be described.

R: Information on the data analysis software and relevant adjustments were added to the text: “Measurements performed with the C-ToF-AMS were analyzed with the data analysis software tool SQUIRREL V1.43; HR-ToF-AMS data were analyzed using SQUIRREL V1.15H – 1.55D and PIKA V1.10H – 1.14D. For the analysis typical settings and corrections were used; for high-mass resolution analysis multiple ions were added to the PIKA ion list.”

10) p. 3530, Line 23: it should be specified whether V or W mode was used for the HR-ToF-AMS measurements.

R: For all HR-ToF-AMS measurements the V-mode was used. We added this information to the text.

11) p.3530, Line 29: how was the vaporizer temperature determined? The thermocouple on the vaporizer is known to not be very accurate, and this temperature has an important influence on the results discussed in the paper. Due to the known limitations of the thermocouple measurement, a procedure has been developed by Aerodyne for more accurate setting of this parameter, see: http://cires.colorado.edu/jimenez-group/UsrMtgs/UsersMtg13/AMSUsersMtg_2012_VapT.pdf Was that procedure or a similar method used for the work reported here? Also a range of 50 degrees C can make a difference for some experiments. The authors should make sure that the vaporizer temperature is given for each one of the experiments for which they report results.

R: The vaporizer temperature was determined using the thermocouple reading of the instrument only. The thermocouple reading was not verified using strictly the Aerodyne procedure described in the reviewer’s comment, however applying similar criteria (like the temperature at which the vaporizer starts glowing or temperatures needed for quick vaporization of certain species), our thermocouple reading seems to be pretty reliable. If not otherwise stated, all measurements presented in this manuscript were determined with a vaporizer temperature of 600 °C. We indicated this in the text in the “measurement setup” section and in the individual sections of the text.

Particle Vaporization Kinetics

12) p. 3531, Line 12: Fig. 2 is similar to Fig. 6 of Jayne et al. (2000), suggest citing that paper here.

R: done.

13) p. 3531, Lines 18-20: a reference should be given for these reactions. If they are speculative, this should be noted.

R: We added references for reactions R1-R3. Reaction R4 (thermal decomposition of ammonium sulfate into ammonia and sulfuric acid) is assumed based on the ions we find in the mass spectra of ammonium sulfate, as now also stated in the text. We also added references for reactions R5 and R6.

14) The meaning of the vertical arrows in the first reaction should be explained. Does this mean that the species evaporate? Then that would mean that the second reaction happens in the gas-phase, but it is not plausible for 4 HNO3 molecules to collide in the gas-phase and react in this way. This also relates to the text on Lines 23-24 that seems to assume gas-phase reactions. The third reaction should be written as 2 NO2 <–> 2 NO + O2.

R: We removed the vertical arrows in the first reaction also in agreement with a comment by reviewer 1. In addition we re-wrote the third reaction according to the suggestion. See also the reply to a related comment of reviewer #1.

15) p. 3531 Line 16-26: this section reads as if gas-phase reactions were most important. However hot tungsten is known to be a good catalyst: for example a search for “tungsten catalyst*” returns almost 2000 records in Google Scholar, most of which appear to concern organic reactions. The potential for reactions on the tungsten surface

should be acknowledged in this section and throughout the manuscript.

R: We added a short general section summarizing the processes that occur on the vaporizer at the beginning of section 3 as suggested in the next comment. In this section we also briefly discussed the possibility of tungsten acting as catalyst for reactions on the vaporizer.

16) Page 3532, Line 1: The authors mention several of the processes that can give rise to signal during the AMS vaporization process, but they do not provide a summary of these processes in one place. For example, at the start of section 3 (just before section 3.1) the authors could have a summary paragraph in which the clearly state the main processes that likely contribute to AMS particle vaporization kinetics including: a) Fast flash vaporization of aerosol species of interest off the AMS vaporizer b) Slow thermal decomposition of species of interest on the AMS vaporizer c) Condensation of flash vaporized species and/or decomposition products on cooler surfaces such as the ionizer surfaces on which they may undergo subsequent slower desorption and further thermal decomposition. d) Particle bounce off the AMS vaporizer followed by slow vaporization/decomposition of bounced particles from cooler ionizer surfaces (or occasionally the filament surface which is hotter). The authors refer to a - c in the discussion but they surprisingly do not mention the contribution of particle bounce (d) at all. Previous work has shown that particle bounce does not significantly affect the vaporization process of NH4NO3 (Cross et al. 2009), but it is expected to affect all the aerosol particles measured in this work including (NH4)2SO4 (Middlebrook et al. 2012) and the other solid semi-refractory aerosols (Matthew et al. 2008). The bounced fractions for some of these species may be quite high, comparable with _70% for PSLs. Thus, it is important the authors should explicitly consider and mention the possible role of particle bounce in the various observations.

R: As suggested by the reviewer we added a short summary at the beginning of section 3, just before section 3.1, summarizing the processes that occur on the vaporizer and in the ionizer. Here we also included the discussion of particle bounce and the possibility of the tungsten vaporizer acting as catalyst: “All AMS measurements are based on the vaporization of individual particles from the AMS vaporizer, a porous tungsten rod with an inverted cone shape (both for improved collection efficiency of the particles), that can be heated up to approximately 800 °C (typical operation temperature: 550-600 °C). When particles impact onto the AMS vaporizer they can either directly bounce off or remain on the vaporizer. The fraction of bouncing particles ranges between approximately 0% and more than 50% and strongly depends on the composition and the phase of the particles with partially or completely liquid particles showing less bounce than solid particles (Matthew et al., 2008, Middlebrook et al., 2012). 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). Particles which remain on the vaporizer are heated by the hot tungsten surface and, depending on their thermodynamic properties and the vaporizer temperature, can flash vaporize, vaporize slowly or thermally decompose during the vaporization process. During contact with the vaporizer surface, the hot tungsten could act as a catalyst and support reactions with other aerosol components or with material on the vaporizer surface. Material that leaves the vaporizer as a consequence of the above-mentioned processes expands into the ionizer volume where it can be electron ionized for subsequent mass spectrometric analysis. Vaporized species as well as decomposition products can condense onto surfaces in the ionizer assembly and will desorb, potentially after further decomposition, from these surfaces depending on the individual temperatures of the respective locations until they finally end up at sufficiently cool surfaces that they are not desorbed anymore or are removed from the ionizer chamber by the pump. These adsorption-desorption processes can extend the residence time of the respective vapor components according to their tendency to stick to the surface (Drewnick et al., 2009).” We limited the discussion of particle bounce to this paragraph and did not discuss bounce for each of the observations because bounce is generally considered as an effect that only results in the loss of a certain fraction of the aerosol for further analysis. According to this assumption it should not have any effect on the observations

discussed here. There is a certain chance that particles which bounced off the vaporizer are collected on other surfaces and vaporize at these locations. However, this effect seems to us very unlikely and not to contribute significantly to the overall signal and is not investigated here. Therefore we did not include it in the further discussion.

17) Page 3532, Line 1: It would be useful along with statements in comment 16 above for the authors to summarize the timescales with which the different measurement modes provide information about vaporization. For example, the single particle measurements take place on timescales of tens of microseconds and average PToF measurements are on timecales of milliseconds. MS open/closed measurements, on the other hand, are typically on timescales of seconds and most likely to reflect the all the vaporization processes mentioned in comment 16.

R: We present measurements performed only in single particle measurement mode and in MS mode. Single particle measurements are simply non-averaged PTOF measurements and therefore provide information on a similar timescale as PTOF measurements. We added a statement about the timescale of the single particle measurement in the first paragraph of this section where the measurements are mentioned first: “For this purpose a C-ToF-AMS was operated at high (83 kHz) pulser frequency in BFSP mode where measurements on timescales of tens of microseconds are obtained.” For the MS mode measurement with extended open and closed times the timescales have already been specified.

18) p. 3532, Line 5-7: The authors are suggesting that NO is the slowest vaporizing component because it does not decompose and it slowly adsorbs and desorbs off the ionization surface. While this is certainly one possible scenario, another likely scenario is that the vaporized HNO3, which is stickier than NO, adsorbs onto the cooler ionization surface and undergoes extensive slow decomposition that gives rise to the slow NO signal. This should at least be mentioned as another possibility. It should also be noted that some form of surface chemistry must be involved, as otherwise the NO+ signal would be expected to decay the fastest if it was present on the gas-phase (or

was the product of gas-phase reactions of the other faster-decaying species), due to its higher thermal speed.

R: We do not suggest that NO vaporizes slowly but that it survives the high temperature conditions longest and therefore can undergo adsorption/desorption cycles on the cooler (but also hot) ionizer walls what results in an extension of residence time in the ionizer. We agree that HNO3 is stickier than NO and would adsorb more efficiently to the ionizer walls than NO. However, we do not see why HNO3 should vaporize off the vaporizer without decomposition but decompose on the much cooler ionizer walls. Even if this is the case it would likely contribute only very little to the overall process since already in the very early phase of single particle vaporization events the fraction of HNO3 in the signal is very low. We do not think that surface chemistry is needed to explain the NO+ signal to last longest. As written above and described in the text physical adsorption/desorption processes are sufficient to explain this. We revised the text to make this clearer: “A possible explanation for the longer appearance of the m/z 30 signal – after the other signals already have decayed (Fig.2a) – is that the NO molecules, as end products of Reactions (R1) to (R3), survive the high temperature condition longest. Therefore they have the potential to stay longest in the ionizer volume, likely further extended by adsorption/desorption to the ionizer walls.”

19) p. 3532, Line 8: Please state at the beginning of this paragraph that the discussion deals with measurements of single particle vaporization events at different ion extraction frequencies. Also mention in this discussion that while faster extraction frequencies would provide a more precise measurement of any given single particle, the choice of extraction frequencies is often limited by the m/z range that is needed for the MS measurements. When slow extraction frequencies that are on the order of vaporization timescales are used, accurate measurements of the average single particle can still be obtained with sufficient particle counting statistics. For ensemble aerosol measurements, the S/N decreases at slower extraction frequencies,but the accuracy of the measurements are not affected if they are referenced to NO3 calibrations performed

under (or scaled to)the same extraction conditions.

R: We stated now that vaporization events are “single particle vaporization events” at the beginning of this paragraph. We also added a statement about the limitation of pulser frequencies due to its relationship to m/z-range. Furthermore, we revised the text to make the effects of small pulser frequencies clearer: “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 very often very small signals (i.e. individual ions) 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 individual ions (e.g. in 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) when the pulser frequency changes. 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.” See also the reply to a related comment by reviewer #1.

20) p.3532 Line 17-18: the statement on the change of the fragmentation pattern of ammonium nitrate as the pulser frequency changes is incorrect. Lower pulser frequencies will result in noisier fragmentation patterns on a particle by particle basis, but since the arrival of the particles is uncorrelated with the pulsing times, ratios of averages using PToF or MS modes will still be correct and not change with the pulsing frequency. If the authors have data that suggests differently, it should be presented here, or otherwise this statement should be removed.

R: This is correct. However, there is a possible effect due to reduction of signals below threshold levels. To make this clearer we revised the text (see reply to comment 19).

21) It should be mentioned that a possible reason to observe an artificial change in

fragmentation patterns would be if the ion-detection threshold is not set properly, as in that case the weaker signals would be discriminated against (Hings et al., 2007). Also in Brute Force Single Particle mode there could be an artificial bias depending on the threshold settings for single particle detection. The latter error should not affect averaging modes such as MS and PToF.

R: We agree with the reviewer and revised the text accordingly. See also reply to comment 19.

22) p. 3532, Line 21: It is important to recommend that since the AMS reports mass concentrations measured in MS mode, the IPP measured from single particle measurements should be checked against ionization efficiencies measured by comparing ensemble MS and CPC measurements before it is used in mass concentration calculations. Also it is standard practice to determine RIE_NH4 using the measured NH4/NO3 ratio in MS mode, rather than using the single particle measurements.

R: This information is important, however a bit out of focus of our discussion here. If we open this discussion we should extend it further to potential particle size or concentration dependences. Therefore we do not include this statement here.

23) p. 3533, Line 1-4: Why do these reactions not include HSO3+ which is the source of m/z 81? Also, as for NH4NO3 and based on the same arguments, the longer evaporation timescales for SO+ and SO2+ relative to the larger sulfate fragments indicate that surface chemistry is important for the smaller fragments. This needs to be mentioned. It is also of interest to note that NH4 fragments desorb more slowly from ammonium sulfate than ammonium nitrate, and as fast as the fastest anion fragments.

R: The reactions R4 – R6 summarize the decomposition of ammonium sulfate as we think it occurs in the AMS vaporizer/ionizer chamber. These reactions are based on the observations (i.e. which ions are observed during measurements of ammonium sulfate) and additional literature information (which is now also cited). HSO3+ ions are regular electron impact ionization fragments of sulfuric acid as already stated in the text

directly below the reactions. In typical AMS sulfate fragmentation patterns and standard sulfuric acid EI fragmentation patterns one finds very similar ratios of m/z 81 and m/z 98. This means that the observed signals at m/z 81 (HSO3+) are likely completely generated by fragmentation of H2SO4 when ionized with electron impact. There is no need to generate HSO3+ in any other way to explain their occurrence in the spectra and therefore these reactions do not include this molecule. We added a statement on the possibility of condensation and slow thermal decomposition of sulfuric acid on the cooler ionizer walls to the text. However, we also included our opinion that likely this effect would only contribute to a very small degree to the overall vaporization event lengths of the ions: "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 condensation of H2SO4 on cooler ionizer walls followed by slow thermal decomposition and vaporization of the decomposition products. However, also in the early phase of the vaporization events H2SO4 makes up only a very small fraction of the vapor molecules, indicating that this species is only a minor fraction of the overall material that leaves the vaporizer. If this small fraction condenses on the ionizer walls and then decomposes and desorbs over extended times it will contribute only to a very small degree to the overall signal. Therefore we do not assume that slow thermal decomposition of vapor material on the cooler ionizer walls significantly contributes to the lengths of vaporization times." Finally, we also mentioned in the text that also the ammonium-related ions have longer vaporization event lengths compared to those from ammonium nitrate: "For ammonium sulfate, generally slightly longer particle vaporization events are observed, compared to ammonium nitrate (Fig. 2c), both for the sulfate-related ions but also for those associated with ammonium."

24) p. 3533, Line 8-10: again this statement is incorrect, fragmentation patterns will not change with the pulser frequency."

R: To avoid an extensive discussion of threshold effects and since the potential change in fragmentation pattern (see discussion above) is not directly related to the differences in vaporization event length we removed this statement.

25) p. 3533, Line 25-28: How are the vaporizer temperatures determined- are they the temperature readouts from the AMS vaporizer thermocouple? Was a NaNO3 temperature calibration performed before these experiments?

R: The vaporizer temperature was determined from the thermocouple reading of the instrument. From our experience we receive relatively reliable information from this approach which are likely as robust as the NaNO3 temperature calibration for our instrument (see reply to comment from reviewer #1). We added this information to the text in the "measurement setup" section: "If not otherwise stated measurements were performed with a vaporizer temperature of 600 °C, which was determined using the thermocouple reading of the instrument."

26) Same section: a recent paper (Docherty et al., 2015) reports results when an AMS was operated in a field study with varying temperature of the vaporizer. The results of that paper appear to be consistent with those of the present one, and we suggest that this is mentioned here.

R: We added the reference to the Docherty at al., 2015 paper to this section.

27) p. 3533, last paragraph: the procedure for setting the temperature of the AMS vaporizer is based on this principle of measuring the size distribution width for NaNO3, and that could be mentioned here.

R: We added this information here: "Conversely, this effect can also be used to select the standard AMS vaporizer temperature by setting it to the value at which size distributions of NaNO3 are just not broadened anymore."

28) p. 3534 Line 9: as mentioned earlier a similar report was given by Huffman et al. (2009).

R: We also added this reference here.

29) p. 3534, Line 10-12: Why was 17 min chosen as opposed to other timescales? It would be useful to point out that this operating condition is way outside the typical AMS operating mode of switching between open and closed modes on the order of 5 seconds. Also, what were the mass concentrations that were used? In the figures these concentrations are quite high (again atypical compared to typical operation). Mass concentrations would likely affect observed timescales as well, with higher concentrations possibly resulting in longer timescales, as an insulating layer might be built up on the vaporizer by the accumulated particle mass. This should be discussed.

R: The timescale (17 min) was arbitrarily chosen. For these measurements 200 data points of about 5s each were collected, which results in approximately 17 min total measurement time. We added a statement that this timescale is way beyond the typical measurement times. The mass concentrations are at a level typical for many laboratory experiments (a few tens to a few hundreds of μg/m3). Since on the vaporizer we observe very fast vaporization even at much higher concentrations we do not expect any buildup of layers and affection of timescales due to the aerosol concentrations used during these experiments.

30) p. 3534, Line 12. I don't understand why 5 seconds is the best possible time resolution. Measurements can be obtained with 1 second time resolution in Fast MS mode (Kimmel et al., 2011), and the AMS is capable of 10 Hz measurements in Eddy correlation mode (Farmer et al., 2011). Perhaps it was the best time resolution at the time the experiments were done, but if so this qualifier should be added.

R: Correct, the 5 second time resolution was the best possible time resolution that could be obtained at the time of the measurements. A statement about this was added to the text.

31) p. 3534, Line 13-17: Why is the NH4NO3 signal increasing in the first two open time periods? Is this due to source variability? Are the signals normalized to the input particle concentration?

R: The signal intensities are not normalized to the input concentration but presented as measured. The increase in signal in the first two open time periods in Figure 3a is likely a result of slightly increasing aerosol mass concentrations during the early phase of this experiment.

32) p. 3534, 2nd paragraph: it is unclear what signal is shown, open, closed, diff, or total. It would seem that the total signal is shown, but this should be clarified. This should also be clarified for Figure 4, and perhaps elsewhere.

R: As indicated in the figure captions of Figure 3 and 4 the time resolved ion signals of the individual ions are shown over time. In this kind of experiments it does not make sense to think in terms of “open”, “closed” or “diff” signals since no quasi-parallel measurement of open and closed is performed and no diff is calculated from these measurements. To make this clearer we added a statement to the introductory sentences: “To investigate the kinetics of particle vaporization in more detail, experiments have been conducted where the beam open and beam closed intervals have been extended way beyond typical operation conditions to approximately 17 min each and the ion signal was measured during this time with best possible time resolution (∼5 s, i.e. one second sampling time, four seconds saving time; this was the best possible time resolution at the time the measurements were performed).”

33) p. 3534, Line 19: The background value of H2O is always high in the AMS, due to the particular vacuum technology used. How does the closed signal that is measured during these experiments compare to typical background H2O in this instrument? (before the experiments started). Otherwise the background H2O is not particularly meaningful for this discussion. Also was the increase in H2O signal when sampling nitrate due to particle-phase H2O (particles were not dried)? Or was it due to gas-phase H2O if the particles were dried?

R: The background value of H2O is always high and a problem in high vacuum systems due to the tendency of water to stick to the walls and slowly evaporate from the

walls which therefore act as a constant source of water in the vacuum system. It is hard to specify a typical background concentration of H2O in the instrument since the actual background strongly depends on the history of the instrument and the kind of measurement performed at the moment. After opening the instrument towards ambient air the H2O background is high and decreases for weeks. When measuring in the lab or in the field H2O background tends to increase. During the experiments we observed H2O background signals in the order of 300 kHz. These values are probably in the upper range of the typical levels, mainly due to the fact that laboratory aerosol was measured with partially high aerosol concentrations. However, the absolute level of the H2O background is not the most important variable here, but the variation of the H2O signals. As presented in Figure 1 all aerosols were dried before analysis. However, for NH4NO3 this does not necessarily mean that there was absolutely no water on the particles. Water will be from the gas phase, from the particles and from the decomposition of NH4NO3.

34) p. 3535, Line 18-22: Since the mechanisms of decomposition are different between the two (as KNO3 cannot make HNO3), it is not clear how the NH4NO3 observations are necessarily related to KNO3 measurements.

R: Also for other nitrates (e.g. KNO3) we observe NO- and NO2-related signals which also come from decomposition products of the nitrate – as those observed for NH4NO3. Of course the chemical pathways that result in these signals are different for the different species. To make this clear we revised the text slightly: “Since quick vaporization of KNO3 occurs at higher temperatures compared to NH4NO3 the thermal decomposition, albeit partially along different chemical pathways, progresses further for this species before ionization.”

35) p. 3535 Line 23 to P.3536 Line 7: the slower behavior of SO+ and SO2+ again suggests that the vaporizer surface plays a larger role for generating those fragments. Alternatively, could the slower fraction of those signals be dominated by particles that bounced and deposited into surfaces colder than the vaporizer?

R: We do not think that the vaporizer surface plays a large role for such effects lasting over many minutes. At the typical vaporizer temperature most of the ammonium sulfate vaporizes within milliseconds from the vaporizer (therefore PTOF measurements of this species are possible). It seems rather unlikely that vaporization from this same surface extends over many minutes – 5-6 orders of magnitude slower. We think it is much more likely that residence time in the ionizer, extended by adsorption/desorption processes from surfaces of various temperatures, is the major reason for these slow signal decays. Also the shape of the signal decay with consecutively increasing decay constants, in agreement with desorption from consecutively cooler surfaces, supports this assumption. As discussed above, bounced particles are generally assumed to be lost for the analysis process. We have no measurements that could provide any evidence for the contribution of signal from bounced particles. Therefore all conclusions using such effects would be highly speculative. Therefore we just mention bounce in the overview of effects occurring in the vaporizer/ionizer system without further discussing this issue. Nevertheless, we acknowledge that dedicated investigations regarding this issue would be desirable.

36) p. 3536, line 14-16: It is not clear that SO2 will stick more efficiently to the ionizer walls than H2SO4. It seems more likely that gas phase H2SO4 that is flash vaporized sticks to the ionizer surfaces and then undergoes slower vaporization and increased decomposition at the cooler ionizer surface temperatures. (NH4)2SO4 is also known to undergo bounce. So, slow vaporization from bounced particles should also contribute significantly to the observations. This should be discussed here in the context of the observations.

R: It was not our intention to imply that SO2 sticks more efficiently to the ionizer walls than H2SO4, but adsorption/desorption processes at the ionizer walls could increase the residence time of the SO2, which is the end product of the decomposition processes. To make this clearer we re-worded the sentence: “The slower decay of the m/z 48 and 64 signals suggests that for the SO2 molecules, which are the end products

of the thermal decomposition reactions (R4) to (R6), the residence times in the ionizer are extended by adsorption/desorption processes at the ionizer walls.” As mentioned above we do not think that H2SO4 surviving the vaporization on the hot vaporizer and then decomposing slowly at the cooler ionizer walls contributes to the overall signal to a large degree. Regarding the potential contribution by bounced particles, see the reply to the previous comment.

37) p. 3536, line 22: The time per half cycle that is typically used when performing ambient measurements, for example, should be mentioned somewhere for reference.

R: We added this information to the text.

38) p. 3536, line 27: The "significant reduction" mentioned in text should be quantified by comparing the PToF and MS measurements for these experiments, if available.

R: Unfortunately PToF measurements are not available for these experiments. Since PTOF data are typically not used quantitatively without scaling by MS measurements and since we do not have information about possible variations of these scaling factors we do not think adding this information here is very useful without further investigations on this topic.

39) p.3537 Line 11, can the authors quantify “not far above.” This information would be quite useful.

R: There is no strict limit of melting points up to which the respective substances can be measured. The lower the volatility at the vaporizer temperature – often reflected by the relative value of the melting point in relation to the vaporizer temperature – the less efficiently a substance can typically be measured with the AMS. To provide some more quantitative information here we defined two groups of species depending on their melting and boiling or thermal decomposition temperatures. Please see also the reply to reviewer #1 for more information.

40) p.3537, Line 15: elemental Hg is a gas, and should be removed from this list.

R: done.

41) p.3537, some of the species mentioned may decompose in the tungsten vaporizer and some decomposition products may partially evaporate be measurable. This possibility should be mentioned. Also, and as discussed earlier in the paper, the vaporizer temperature can be increased to at least 750-800C, which may allow the measurement of additional species. This should be mentioned as well. (Custom vaporizers to reach higher temperatures have also been demonstrated (Svane et al., 2004)).

R: The possibility of decomposition of substances is now explicitly mentioned in the text. We also added the comment about increased vaporizer temperature: "At higher vaporizer temperatures (up to 800 °C is possible with the standard vaporizer) these substances can likely be measured more efficiently (albeit with the potential of increased decomposition) and possibly additional substances can be detected with the AMS."

42) p. 3538, Line 29: have size distribution measurements been attempted with the fast-vaporizer ZnI2+ fragment that was discussed earlier?

R: No, such measurements have not been attempted. Since ZnI2 is only a minor fragment, measurements that would provide robust results would probably need very high concentrations of ZnI2 aerosol which would contaminate the instrument for very long times. We therefore refrain from doing these measurements now.

43) p.3539, Line 7: "measured" should be changed to "difference-mode" to clarify that this is a problem with that mode. I.e. when species evaporate slowly, the assumptions that underlie the difference mode are not true, and thus the concentrations reported are wrong (and this is not surprising, it is expected). We suggest explaining this more clearly in this section. Also, the method of Salcedo et al. (2010) can be used to quantify semi-refractory species by using the open and closed signals directly. We suggest discussing that method here briefly and referring to readers to that publication for further details.

R: We revised the text according to the reviewer's suggestion. We also added an explanation of the difference mode measurement and the underlying assumptions as well as the reference to the Salcedo et al. method: "When increasing the measurement half-cycle lengths from 0.5 s to 30 s the mass concentrations as calculated from the difference signal increase by 50% for the m/z 64 (Zn+) and by 80% for the m/z 127 (I+) signal showing that variations in measurement cycle length will have a significant effect on the mass concentrations determined in regular MS mode measurements (difference spectrum with 5-10 s half-cycle length). This mode is based on the assumption that during the beam open phase the sampled aerosol flash-vaporizes and is measured completely and during the beam closed phase only the instrument background is measured. If aerosol-related signals decay slowly over time intervals longer than the half-cycle length this assumption is not valid anymore. A method to estimate the complete aerosol signal of such substances from the beam open and beam closed signals was presented by Salcedo and coworkers (2010)."

44) p. 3539 L16-19, again it should be noted that this change only concerns the difference mode, but that additional analyses may improve the results.

R: We added the information that this only concerns the regular MS mode measurements.

45) p. 3540, Line 5-7: The NaCl that is being vaporized off ionizer surfaces also likely comes from bounced particles. This should be mentioned.

R: As discussed further above we do not have any evidence for bounced particles to be collected on ionizer surfaces and contributing to the overall signal. Actually, if this would be the case in this experiment where during measurements of NaCl the vaporizer temperature (and as a consequence the ionizer surface temperatures) was increased, aerosol collected and accumulated on the ionizer surfaces should have generated a very large signal during the heating process which we did not observe. Therefore we do not discuss these effects before having performed dedicated experiments to investigate them.

46) p.3541: the dash should be removed from the Y-axis labels, as it appears to indicate "minus the ratio

R: Figure 5 was changed according to the reviewer's suggestion.

47) Line 3541, Line 6-10: How do you distinguish between slow decomposition and vaporization processes off the oven and slow adsorption/desorption processes off the ionizer surfaces? It is also possible that FeCl3 sticks to ionizer walls and slowly decomposes at the lower temperatures as opposed to FeCl2, Fe, and FeCl2 sticking to ionizer walls and slowly desorbing.

R: We agree with the reviewer that different processes could occur and our measurements are not capable of distinguishing between them. Therefore we do not make any assumption on the exact nature of the processes which result in the observed behavior of the various ions. We only state that "... accumulation in the ionizer volume builds up ... for the ions ...". We think adding various possible explanations which processes could cause this behavior would not improve the manuscript and therefore leave the text here as it is.

48) p.3541, last paragraph: using the "extended RIE" idea carries the risk that its value will only be valid for the same conditions where it was acquired. The alternative quantification method of Salcedo et al. (2010), that uses both the open and closed signals (rather than only the difference signals) and takes the slow evaporation into account directly, should also be mentioned here.

R: The fact that the "extended RIE" is only valid for the conditions where it was determined is already stated in the text. We added the reference to the Salcedo method also here.

49) p. 3542, Line 20: It is not clear from Table 2 that there is a relationship between RIE and c/o ratios. The authors should clarify what they mean.

R: We re-worded the text to make clearer what we mean: "Therefore both types of RIE values provide only information on the magnitude of the correction factor needed to obtain realistic aerosol mass concentrations for these semi-refractory species. However, the comparison between RIE values and associated c/o ratios shows that even though very large c/o ratios are associated with very small RIE values and vice versa, no strict relationship between these two variables is observed."

50) p. 3542, Line 26: Since this is the first main discussion of matrix effects involving reaction of two aerosol components with each other on the oven, it would be useful to see an example of the data that the authors are referring to. If the authors prefer not to show the data, I suggest removing the reference to matrix effects after line 26 on this section.

R: According to the reviewer's suggestion we added a paragraph presenting some of the data. For this purpose we also added another panel to Figure 5. The revised text reads now: "Finally, several experiments have provided evidence for matrix effects where as a consequence of chemical reactions of the semi-refractory aerosol component with a matrix component (ammonium) significant changes in vaporization kinetics (i.e. in c/o ratios) were observed, which in turn result in changes in RIE. For the measurements of RIEmix the metal chlorides have been mixed with different ammonium salts in the solution in the atomizer. In the mass spectra, in addition to the signals associated with the salts in the sample, also signals from adduct formation were observed like FeClxNH3+ in the FeCl3/(NH4)2SO4 mixture or AlClxNH3+ in the AlCl3/(NH4)2SO4 mixture. Furthermore, we observed shifts in relative signal intensities in the mass spectra of internal mixtures compared to those of pure substances. While in the mass spectra of pure SrCl2 particles the ion 88Sr+ dominates the spectrum and is about three times as intense as the 88Sr35Cl+ ion; in the mass spectrum of the mixture with NH4Cl the relation of the intensity of these two signals is approximately inverted. This apparent change in ion generation processes is also reflected in c/o-ratios. While for the pure substance both ratios show similar behavior and are in the order of 100% (Figure 5b), for the mixtures with ammonium chloride the SrCl+ signal shows reduced c/o ratios while that of the Sr+ signal is largely unchanged (Figure 5c). Similar behavior was observed for the SO+ (m/z 48) and SO2+ (m/z 64) signals of K2SO4: c/o ratios for both ions were in the order of 30% for the pure substance, while ratios of about 11% were found for these signals in the measurement of mixtures. Apparently, in the mixtures a quicker vaporization of the aerosol substances occurs, compared to the pure substances. In the measurement of FeCl3 we also observed large changes in the mass spectra when mixtures of FeCl3 with (NH4)2SO4 were measured. At constant FeCl3 concentration in the aerosol an 8-fold increase of the 35Cl+ signal was observed in the mass spectra of the mixture while the intensity of the 56Fe+ signal was reduced by a factor of 6.5, reflecting strong changes in measurement efficiencies for these substances. Taking all this into account, RIE values for semi-refractory components determined from internal mixtures with other species (RIEmix) should not be generalized for mixtures with different components without further investigation of these effects."

Chemical Reactions on the vaporizer

51) p. 3544 Line 26 and 3545 lines 11-13: the percent increases in the CO2+ signal have no meaning, since they depend on the gas-phase concentration of CO2 as well as on the particular concentration of particles used in these experiments. We suggest removing these values and instead stating that the increases were clearly measurable. This focuses the discussion on the increase in measured O/C etc., which is the important result here.

R: In the text we already discuss that the CO2+ signal is from both, the carrier gas as well as from the aerosol particles. We also discuss the separation of these two contributions. We added the information about the increase of the absolute CO2+ signal (including aerosol particle and carrier gas contribution) to show that this increase is significant and large, even if the carrier gas contribution is included. Since we think this is relevant information we leave it in the text.

52) p. 3545. Line 5-7: It would be useful to have an example of these PToF data as a supplementary figure.

R: Since only the confirmation that the changes in CO2+ signals are associated with particle-related CO2+, i.e. that a CO2+ peak was observed at a particle time-of-flight where aerosol particles and not gas phase is expected, and no further processing of these data was performed we refrain from adding a supplement just for this measurement. We are happy to provide data to interested readers upon request.

53) p. 3545. Line 19-21: It would be useful if the authors note here that the increases in O/C that are observed in these studies are very small compared to the increases of interest for atmospheric aerosol particles.

R: The fact that the observed increases in O/C ratios are very small compared to the changes and differences observed in ambient measurements was already discussed in the Discussion section of the manuscript. Nevertheless, we added this statement also here: “However, it must be noted that these increases in O/C ratios are very small compared to the changes or differences typically observed in ambient measurements.”

54) p. 3546, line 23: Why does 80 go up with background H2O if Reaction R5 is shifting towards reactants?

R: In agreement with similar comments of reviewer #1 we revised the text associated with the ammonium sulfate / RH experiments. The reference to Reaction R5 is now removed from the text. The revised text reads now: “For ammonium sulfate no significant changes of relative signal intensities (related to the intensity at m/z 64) were found when the aerosol RH was increased from 1.5% to 85%; for the various ions, average changes of relative signal intensities ranged from -4% up to +3% with an average uncertainty of ±19%. Only, when correlating the relative signal intensity with the H2O ionizer background signal (beam closed m/z 18, H2O+, related to the amount of water introduced into the instrument during recent measurements) a significant increase in relative m/z 80, 81, and 98 signal intensity with increasing water instrument background level was found. From linear regression of the data an increase of (+38±18) % was found for the m/z 80 signal, of (+27±16) % for m/z 81, and of (+28±17) % for m/z 98 over the range of water vapor background signal levels (303-322 kHz) measured within this experiment. These results suggest that also the efficiency of sulfuric acid decomposition is somehow related to the presence of water in the process, however, this dependence results in very small and typically negligible changes in fragmentation patterns."

55) p. 3546, line 23-24: Given the fact that the changes are not statistically significant, it seems that a more reasonable conclusion is that carrier gas humidity does not have a strong observable effect on the observed sulfate mass spectra.

R: We agree with the reviewer's comment. Therefore the revised text (see reply to comment #54) contains exactly this conclusion.

56) p. 3546, line 25: Was there evidence of increased collection efficiency for the SO4 with increased RH? This is expected from Allan et al. and Matthew et al. measurements.

R: Yes, we also observed an increase in absolute signal intensity in the ammonium sulfate measurements with increasing RH, likely also associated with improved CE, in agreement with Allan et al. and Matthew et al.. We included this information in the text: "Experiments with NaCl particles did not show any dependence of the relative intensities of the signals in the associated mass spectra from carrier gas RH; however, the absolute signal intensity increased four-fold when increasing RH from 1.5% to 85%, likely due to an increase in collection efficiency on the vaporizer, similar to what has been observed for ammonium sulfate in our measurements and previously (Allan et al. 2004a, Matthew et al. 2008)."

57) p. 3547, Line 1: It would be useful if the authors provided an introductory sentence that specified whether the chemical reactions discussed in this section are observed only for semi-refractory species or both semi-refractory and non-refractory species.

R: We did not find any evidence for the fact that chemical reactions on or with the vaporizer are limited to non-refractory or semi-refractory species. Therefore we do not see how adding a sentence about this here would improve the text and we did not include such a sentence which we think would interrupt the reading flow.

58) p. 3547, line 1-4: Why do you not show the contrast between HR and UMR spectra for these municipal waste incinerator? The non-organic signals should clearly split out from the organic signals in HR.

R: The purpose of showing the mass spectrum of the waste incinerator was to present the result of simply applying the standard UMR analysis to an "exotic" aerosol. For us (at the time of the measurement) this was the first indication that the AMS can potentially measure many more substances than it was advertised for. We did not present the full HR spectrum of the same measurement but only a cutout of this spectrum (Fig. 6b) because presenting the full HR spectrum would probably not look much different from Figure 6a (due to image resolution limitations). There was virtually no organic signal in the exhaust of the waste incinerator (the measurements were taken from the stack, not in the vicinity of the facility). As shown in the cutout there is no organics-related signal between the WO2Cl2-related signals.

59) p. 3547, Line 7: It is useful to more clearly point out that even though UMR does not allow for separation of the metals from organics, in practice there are several methods that can be used to identify and confirm the contribution of semi-refractory species to the signals at these m/zs. These include: unusual spectra with signal at m/zs that are not typical for organic species, isotope patterns that can be used to identify the presence of specific elements, and, as discussed in this manuscript, large âËĞDËĞE ratios that are characteristic of semi-refractory behaviour.

R: We added some text to clearly point out that under favorable conditions UMR spectra could provide some information about "unusual" substances in the aerosol: "It must be noted, that under favorable conditions (i.e. when the contribution to the mass spectrum is sufficiently large) ‘unusual’ substances could also be identified in unit-resolution mass spectra from their intense signal at m/z where no strong organics-related signals are expected, from isotope patterns or from large background signals, characteristic for semi-refractory substances.”

60) p. 3547, Line 13: Are these effects only observed with semi-refractory chlorides? Are similar observations seen for NH_4Cl? It would be useful to specify the difference if possible.

R: As stated in this sentence, these effects are observed for both, the metal chlorides and NH_4Cl. There was no difference observed (besides the different yields as specified further below) as indicated by this sentence: “. . . is a general feature when measuring Cl-containing aerosol species.”

61) p. 3547, Line 15: an indication of the magnitude of the observed effects is needed. Are these WO_2Cl signals 50%, 1%, 0.01% of the main peaks observed for those species? The reactions are interesting, but their impact on atmospheric measurements is limited unless the fractional signal is substantial.

R: We calculated the fractional contribution of the WO_2Cl_2-related signals to the total mass spectra. These values are in the range from 0.04% to almost 20%. All values are provided in the additional table (Table 4) and the range is provided in the text: “The fractional contribution of the WO_2Cl_2-related signals to the mass spectrum depends both, on the yield and on the efficiency of vaporization of the respective species. For the substances investigated here, WO_2Cl_2 contributed between 0.04% (NH_4Cl) and 19% ($CuCl_2$) to the total mass spectra (Table 4).”

62) p. 3457, consistent with what is reported here, Jimenez et al. (2003) reported the detection of MoO^+ and MoO_2^+ when sampling particles containing iodic acids into an AMS, that had an older Mo vaporizer, and attributed them to reactions between particle materials and the vaporizer.

R: Thank you for this valuable comment. We added this information and the reference to the text.

63) p. 3547, Line 17: a reference or other supporting information is needed for the production of WO_3 in the vaporizer, otherwise this seems like a unsupported hypothesis. What is the source of the O_2 thought to be, given that the WO_2Cl signals are still observed when sampling aerosols under argon? Is it O_2 adsorbed to the vaporizer surface, or from remaining from previous compounds sampled?

R: We added a reference for the production of WO_3 on the vaporizer. The fact that WO_2Cl_2 signals are still observed when argon is used as carrier gas suggests that either the small amount of remaining oxygen in the system is sufficient to keep up the WO_3 production or that there is a WO_3 reservoir which was not depleted during the measurements.

64) Is this slow corrosion of the vaporizer a cause of concern in the use of the instrument? Can the authors use the range of RIEs determined here to estimate the mass lost from the vaporizer? I someone was doing these experiments 24/7, would it take a month, a year, or a century to corrode enough vaporizer material to be a concern?

R: Thank you for this comment! We made the calculation and the answer is a clear no! From the WO_2Cl_2 yields determined in this work, from the typical conversions of measured mass concentrations into ions per second and from the ionization efficiency one can estimate that approximately 1.4E-11 g W is removed from the vaporizer per hour when measuring a chlorine concentration of 1 μg/m3. For the size and density of the vaporizer this translates into the continuous measurement of 1000 μg/m3 of Cl in the aerosol for about 1400 years to remove one mm of the tungsten vaporizer. We added a statement to the text that the removal of material is negligible: “The generation of WO_2Cl_2 signals in the measurement of Cl-containing aerosols is a corrosion process of the vaporizer. Estimating the amount of material removed from the ionizer from the WO_2Cl_2 yields and typical ionization efficiencies shows that the removal of tungsten from the ionizer is completely negligible and that it would take years of continuous measurement of highly concentrated aerosol to remove a single micrometer of the vaporizer material."

65) p. 3549, Line 1: $FeSO_4$ is not listed among the sulfates potentially detectable by the AMS in the Table.

R: As described in the text $FeSO_4$ apparently decomposes and Fe forms a refractory substance which likely remains on the vaporizer. Therefore the iron in this substance it is not measurable with the AMS (as also described in the text). Since the table lists elements which are measurable in different types of chemical compounds, this is the reason why it is not included in the Table of substances which are measurable.

66) p. 3549, Line 7-8: what is the magnitude of those signals, relative to the nitrate peaks?

R: The contribution of the nitrate-related signals to the mass spectrum is about 1060 times larger than those of the FeCl/$FeCl_2$ signals. We included this information in the text: "Exactly this kind of effect was observed in measurements of $Fe(NO_3)_3 \cdot 9H_2O$ particles with the AMS: besides intense nitrate-related signals also small but clear (about 0.1% of the nitrate-related signals) ion signals of $FeCl^+$ (m/z 91, 93) and $FeCl_2^+$ (m/z 126, 128, 130) were observed in the mass spectra."

67) p. 3550, Line 15: It is known that vaporizer temperature as well as heater bias and instrument tuning can affect sensitivity to surface ionization. In practice, the heater bias is often tuned while monitoring the K^+ signal to limit the instrument sensitivity to surface ionization. Was the heater bias adjusted to investigate the efficiency with which surface ions were detected?

R: It is known that the heater bias voltage affects the efficiency with which ions from surface ionization are transmitted into the mass spectrometer. In our experiments we investigated the behavior of the instrument under regular measurement conditions.

Therefore we did not adjust the heater bias voltage during these measurements, which is now stated explicitly in the manuscript: "Experiments to investigate the surface ionization process support the above-mentioned picture. Since the efficiency of K^+ ions from surface ionization to be transported into the mass spectrometer strongly depends on the setting of the heater bias voltage, this setting was kept constant during these investigations."

70) p. 3550, Line 29: Please specify what is meant by "the assumption of the above-mentioned separation of vaporization and surface ionization".

R: Since this information is not essential for the conclusions of the manuscript we removed the complete sentence.

71) p. 3551, Line 13: should it be a decrease on the work function, rather than an increase?

R: No, the influence of chlorine with the tungsten surface has the capability of increasing the tungsten work function. This is also in agreement with our observation since increased tungsten work function increases the efficiency of surface ionization according to the Saha-Langmuir equation in agreement with what we observed in our measurements. We added a reference where the chlorine effect on work function is shown.

Discussion

72) p. 3551, Line 21-24: As discussed above the ratios of the different ions will not be affected by the pulsing frequency, other than due to an increase of the noise. We suggest restating the last sentence as follows: 73) "Since these vaporization timescales are often on the timescale of extraction pulser periods, single particle measurements and and associated IPP values must be obtained with sufficient particle statistics to accurately capture the average single particle vaporization event."

R: We revised the sentences along the suggestion of the reviewer: "The standard AMS species (ammonium nitrate, ammonium sulfate, organics) vaporize very quickly from the AMS vaporizer. Differences in vaporization event lengths were observed for these species which are likely associated with the residence times of various decomposition products in the ionizer. Since these vaporization timescales are often on the order of the extraction pulser periods, single particle measurements and associated IPP values must be obtained with sufficient particle statistics to accurately capture the average single particle vaporization event."

74) p. 3352, Line 1: please quantify "not well above".

R: In the results chapter we introduced two groups of substances with clearly defined temperature limits. We added the upper temperature limit of these groups (Group II) here: "From our experience, the melting point of a species can serve as a rough indicator: if it is not well above (approximately 200 °C) the vaporizer temperature one can expect that the substance can be measured with the AMS."

75) p. 3552, Line 7: is it possible that for some species size distribution measurements are possible using some m/z and not others? It seems that for many species different fragments exhibit very different timescales, so just because some fragments show a slow evolution it does not mean that all fragments do.

R: We did not perform measurements in PTOF mode for such species and therefore do not have any information whether for some of the ions size distribution information would be available due to short vaporization timescales. We do not exclude this possibility, but we also do not have any indication that this is the case. However, the sentence in the text only states that in case of slower vaporization no size distribution measurements are possible; this is not in contradiction to the possibility of size distribution measurement using other ions from the same aerosol component if these ions show quick vaporization.

76) p. 3552, Line 10: the alternative quantification method using the open and closed signals (Salcedo et al., 2010) mentioned earlier should be more robust than using the difference signals, and can be mentioned here as an alternative.

R: The Salcedo et al. (2010) method is more robust towards variations in vaporizer temperature or measurement cycle frequency; however, the fact that for similar c/o ratios very different RIE values are observed shows that a method which is based on closed and open signal intensity is not necessarily robust for different aerosol components. Also the observation that as a consequence of matrix effects very different c/o ratios can be observed for a certain component shows a limitation of this approach. We therefore mentioned the Salcedo et al. (2010) method here, together with some additional information on the potential limitations: "An RIE value determined for a certain semi-refractory species in the laboratory is only valid for the applied vaporizer temperature and measurement cycle frequency. An alternative quantification method for semi-refractory species using beam open and beam closed signals (Salcedo et al., 2010) is less susceptible to these instrumental parameters. Our measurements have shown that RIE values determined for semi-refractory species are also dependent on the particle matrix, i.e. the components internally mixed with the target substance, and on the vaporizer history, i.e. the previous measurements with the instrument. Since these matrix effects also affect c/o ratios, the quantification method based on the beam open and beam closed signals (Salcedo et al., 2010) could also be impacted by them. Also, since for a given c/o very different RIE values are observed, c/o alone seems not always to be a sufficient basis for reliable quantification of such species. As a consequence, unless an instrument is carefully calibrated with the species and particle mixtures of interest, such semi-refractory components are only quantifiable with large uncertainties."

77) p. 3352, Line 22: suggest replacing "under general conditions" with "unless an instrument is carefully calibrated with the species and particle mixtures of interest".

R: We revised the sentence as suggested, see reply to previous comment.

78) p. 3553, Line 7: It is important to specify that in environments with large concentrations of semi-refractory aerosol, metal signals can appear at m/z's that are typically assigned as "organic" in UMR spectra. In cases where HR capability is available the

metals can be readily separated from organic species. However, even in the absence of HR capability, the existence of peaks at atypical organic m/zs and isotope patterns can be used to recognize this misidentification. Also, large closed to open ratios can be used to confirm semi-refractory behaviour.

R: We included the information on the various possibilities to identify such “unusual” species in the mass spectra in the text: “In measurements in the exhaust of municipal and hazardous waste incinerators we observed strong signals of multiple semi-refractory components like metal halides and WO2Cl2 from reaction of particulate Cl with the oxidized vaporizer. Most of these signals were observed at nominally organics-related m/z. When the contribution to the mass spectrum is sufficiently large, ‘unusual’ substances could be identified in unit-resolution mass spectra from their intense signal at m/z where no strong organics-related signals are expected, from isotope patterns or from large background signals, characteristic for semi-refractory substances; in high-mass resolution spectra such species can be readily separated from organics signals. Under conditions where essentially no organic material is in the aerosol (e.g. due to complete combustion) or where very large Cl concentrations occur, ion signals from “unusual” aerosol components which are not correctly identified by in-depth inspection of the mass spectra can dominate the total mass spectrum and lead to a distorted picture of the aerosol composition.”

79) p. 3553, Line 10-15 and 25-end: here the magnitude of some of the effects are finally quantified. This information would be more useful when those experimental data are being presented, otherwise it is confusing when isolated in this discussion section.

R: We think that the Discussion section is the right place to put the observations from the Results section into a larger perspective and to discuss actual impacts of the observed processes in real applications of the instrument. This is why we included the comparison of the magnitude of the effects with the magnitude of observations in real-world measurements in this section. However, we also extended the quantitative information on both types of effects also in the results section as specified further above

(comments 53 & 61).

80) p. 3553, Line 20: I suggest deleting the line "chemical reactions of particle components with oxygen or water in the carrier gas or with components from previous experiments which were accumulated on the vaporizer can result in ion signals in the mass spectra which do not reflect components of the measured aerosol" since the data from this experiment does not strongly support it.

R: We agree that the presented data do not strongly support that water in the carrier gas results in changes in the mass spectra. Therefore we removed this statement here. However, we think that our experiments showed that oxygen in the carrier gas can lead to partial oxidation of organics and that after conditioning of the vaporizer signals can appear in the mass spectra which do not reflect the actually measured aerosol. Therefore we leave the latter statements in the text.

81) p. 3554, Line 7: From the results in this manuscript, it looks as though the statement that "the AMS vaporizer does not always behave inertly towards particles" should be qualified to specify "semi-refractory particles" since the experiments do not show this effect strongly or clearly for non-refractory particles. In fact, the long vaporization timescales of the semi-refractory species (as opposed to the shorter timescales of more non-refractory species) likely contribute to the observed lack of inertness.

R: As mentioned above we also observe chemical reactions with the vaporizer surface when measuring certain non-refractory components like e.g. NH4Cl or when we observe oxidation of organic species. Therefore we do not think that it makes sense to limit this conclusion to semi-refractory species only. We already included the limitation of this statement by stating that the vaporizer “not always” behaves inertly. This leaves sufficient space for particles not to interact with the vaporizer chemically. The fact that most of the “normal” ambient measurements are not affected by these effects is already stated below.

82) p. 3554, line 15:This line should also include a reference to particle bounce as well

as slow decomposition of vapors of cooler ionizer surfaces.

R: As mentioned above we do not have any evidence for bounced particles to stick to ionizer surfaces (which are less well suited to collect particles than the vaporizer). Therefore we treat bounced particles as they are generally treated in the AMS community: as particles lost for further analysis. Furthermore, we find it rather unlikely that material vaporizes on the hot vaporizer without decomposition and then decomposes on cooler ionizer surfaces to a sufficiently large degree that the measurements are impacted. However, as the statement is written at the moment it does not exclude this possibility.

83) p. 3554, Line 15-17, again this refers to the incorrect assumption that pulsing frequency biases the averages of the ion ratios.

R: We agree that pulsing frequency does not bias the averages of ion ratios as long as no thresholding effects occur. This can easily be the case in BFSP single particle measurements where an ion threshold is used to identify particle evaporation events. Therefore we re-worded this sentence accordingly: “For slow ion extraction frequencies into the mass spectrometer (i.e. for the HR-ToF-AMS) these differences can cause different single particle measurement efficiencies for the different ions in addition to generally reduced efficiencies. Therefore measurements should generally be performed with highest possible ion extraction frequencies of the mass spectrometer and with the same extraction frequencies as used for calibration.”

84) p. 3554, Line 25-26: While it is possible that the end products of the thermal products can stick with some probability to the ionizer walls, particle bounce and slow decomposition of adsorbed species on the cooler ionizer surfaces are probably more likely to play a role. Since the experiments that have been performed cannot distinguish between these mechanisms, they should be mentioned.

R: We added slow thermal decomposition of adsorbed material on the ionizer walls as possible alternative explanation for this behavior to the text: “An alternative explanation

for this behavior could be slow thermal decomposition of adsorbed aerosol components on the cooler ionizer walls.” We do not think that bounced particles can be collected efficiently on the ionizer walls. If this would be the case we would rather expect less thermal decomposition from the material that vaporizes at these cooler temperatures instead of more decomposition. Since we already included bounce as an effect occurring on the vaporizer in the summary at the beginning of section 3 and since we do not think (and do not have any evidence for it) that this effect affects the mass spectra or the vaporization kinetics, we did not include it here again.

85) p. 3555, Line 15: The data does not show any clear influence of carrier gas or humidity on the mass spectra. It is more accurate to say that these effects were investigated and they were not observed to be significant compared to the uncertainties of the measurements.

R: We revised the text to better reflect the observations. We now state that no significant changes have been observed when changing carrier gas RH. The statement on oxidation of organic compounds is unchanged. The paragraph reads now: “Experiments with argon as carrier gas and with different carrier gas humidities have been performed to investigate possible chemical reactions at the vaporizer. When varying the carrier gas RH, no significant changes in relative peak intensities of ion signals in the mass spectra have been found. In measurements of non-oxygen containing aliphatic and aromatic hydrocarbons small amounts of oxidation have been observed, resulting in O/C values in the range of 0.0016 to 0.018, i.e. within the uncertainty of typical ambient O/C ratio measurements.”

86) p. 3556, Line 2: is there any evidence that the RIE of the non-refractory species can change due to these “conditioning” effects? That would be quite surprising. Or are the authors referring to the “apparent RIEs” of the semi-refractory species? This should probably be clarified.

R: Yes, we are referring to the extended RIEs here. To make this clearer we re-worded the text: “Generally, such conditioning of the vaporizer material does not only generate a potential reservoir for ions in mass spectra of future measurements but can also change the ‘apparent’ relative ionization efficiency of some species and thus the efficiency of measurement of these species with the AMS.”

87) p. 3556, Line 7: please add "when semi-refractory aerosol species can be significant." at the end of the last sentence.

R: We revised the text according to the reviewer’s comment: “While the effects observed in these experiments will not have a significant influence on general ambient measurements of continental or urban aerosols, they can significantly affect the mass spectra under certain conditions like in measurements of laboratory aerosols, probing of anthropogenic sources or in the measurement of remote marine aerosols, when semi-refractory aerosol components can be significant.”

Minor items, grammar, spelling etc.

p. 3257, Line 9: suggest changing “and with subsequent” to “and in later experiments with”. Otherwise a reader may think that SI and EI happen sequentially in the same experiment.

R: done.

p. 3528, Line 29: suggest removing the word “mainly.” This depends on the interests of the user. It is true that semi-refractory species can act as contaminants for determining other species, but if the user is interested on them, then that’s not an issue.

R: We removed “mainly”.

p. 3549, Line 18: the word “veritable” seems out of place here.

R: We removed “veritable”.

Figures

Figure 2: Please specify vaporizer temperature used for the measurements shown in 2a,2b,and 2c in the caption.

R: done.

Figure 3: Please include vaporizer information in caption. Why are NH4+ ions not shown?

R: We added the vaporizer temperature to the caption. NH4+ ions are not shown because we wanted to focus on the behavior of the nitrate- and sulfate-related ions and keep the figure as clear as possible.

Figure 4: It would be more appropriate to show the trends of individual ions in units of Hz rather than mass concentrations which require knowledge of appropriate RIEs for each ion.

R: We converted the data shown in Figures 3 & 4 into units of Hz and revised the Figures according to the reviewer’s comments.

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

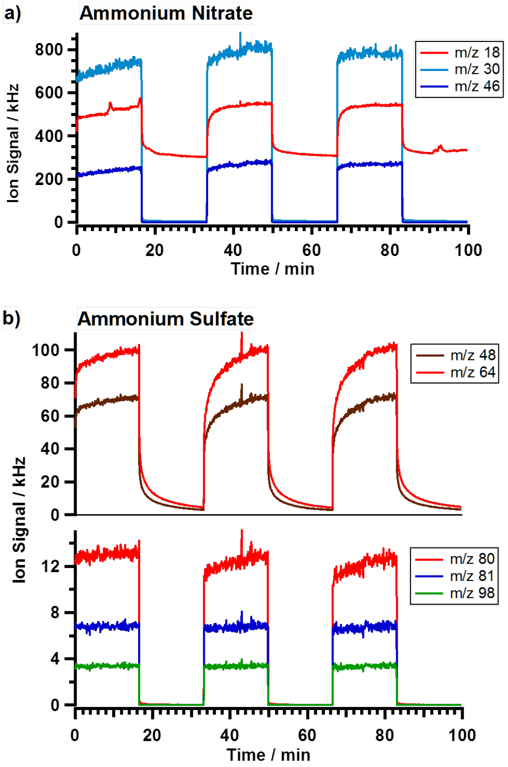

Fig. 1. new Figure 3

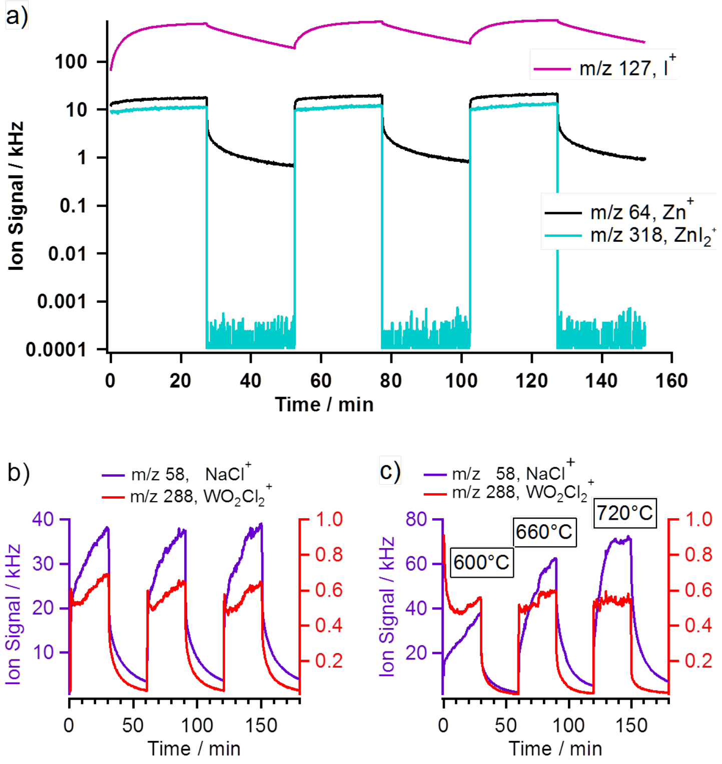

Fig. 2. new Figure 4

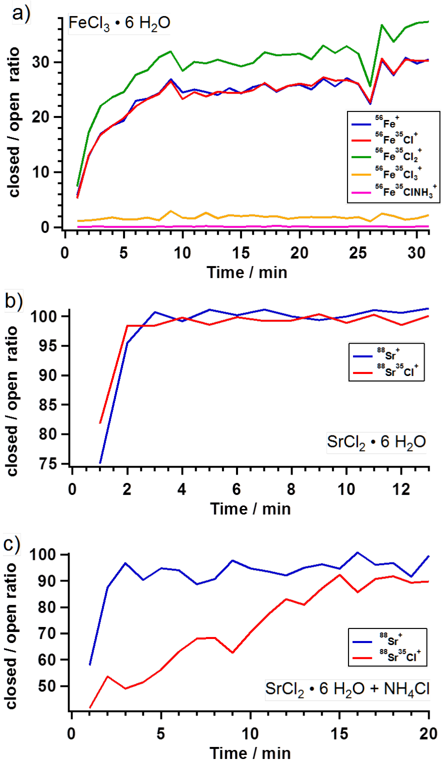

Fig. 3. new Figure 5