

**Response to reviewers for the paper “Evaluation of the new capture vaporizer for Aerosol Mass Spectrometers (AMS) through laboratory studies of inorganic species” by Weiwei Hu et al.**

We appreciate the reviewer’s comments and support for publication of this manuscript after minor revisions. Following the reviewer’s suggestions, we have carefully revised the manuscript. To facilitate the review process, we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**).

**Anonymous Referee #1**

General comments:

**R1.0** In their manuscript “Evaluation of the new capture vaporizer for Aerosol Mass Spectrometers (AMS) through laboratory studies of inorganic species”, Weiwei Hu and coauthors present results from extensive characterization measurements with the new capture vaporizer for the Aerosol Mass Spectrometers. The capture vaporizer (CV) is designed to reduce losses by particles bouncing off the AMS vaporizer. This is achieved by its geometry which helps directing bounced particles into a cavity where they have several additional chances to interact with the hot vaporizer surface. In their manuscript the authors investigate the impact of this vaporizer on thermal decomposition of inorganic aerosol components and associated changes in fragmentation patterns, on collection efficiency for various inorganic aerosol types, and on the size distribution measurement capabilities for such aerosols. In addition the influences of particle beam position on the vaporizer and of vaporizer temperature on such effects are studied.

The development of the capture vaporizer is an important step towards more precise aerosol mass concentration measurements with instruments from the AMS family.

For reliable measurements applying this vaporizer the potential influences of this device onto various features of the measurements (e.g. quantification or size distribution measurements) need to be well known. Therefore I strongly recommend publication of such investigations and I think Atmospheric Measurement Techniques is an adequate journal for this purpose. A large variety of

systematic measurements has been performed thoroughly and provided important information on the performance of the capture vaporizer. The authors have shown how the capture vaporizer increases fragmentation of several inorganic molecules and the collection efficiency of some aerosol types. Furthermore, with the capture vaporizer measured particle size distributions are broadened. While the measurements and data analysis seems to be performed carefully and systematically, the interpretation and the presentation of the results are not satisfying. Several of the conclusions or interpretations of the observations contradict each other or do not completely agree with the observed trends in the data. Some of the conclusions seem to over-interpret the observations and include results from other measurements (from future publications) to end up with statements that go beyond the observations of this study. In many places the text is written rather lax, more resembling laboratory slang than a scientific publication. I have the impression that the text is rather long for the amount of information conveyed and could be shortened somewhat without losing information. I find it rather unsatisfying that here already the second paper on the new AMS capture vaporizer is presented and still many important observations are shifted to the next paper on this device. Why have not internal mixtures of different inorganic and/or inorganic and organic species have been investigated but only statements like that for mixtures of species one would expect better performance are made? I strongly support the publication of this important work. However, I suggest that the authors shorten the manuscript by leaving out repetitive information. The wording should be improved to avoid “laboratory slang” (see comments below). Conclusions which are contradicting each other or which are not in agreement with the measurement results should be avoided (see comments below).

**A1.0:** We sincerely thank the reviewer for his/her detailed review and useful comments, which have helped us improve the quality of this manuscript. All of the items mentioned in this initial comment are addressed below in response to the more specific comments below, in particular R1.1, R1.11, R1.13, R1.20, R1.28, R1.44-R1.50, R1.56, R1.59-R1.60, R1.71, R1.84, R1.90, R1.108.

We note that for an instrument as complex as the AMS, with so many relevant measurement features and details, and that is used to analyze many types of aerosols in both laboratory and field studies, it is impossible to carefully document all the effects of a change as major as the CV in a single paper. The present paper already has 87 figure panels and tables. The paper about organic aerosols that complements this one has a comparable number of figures and tables, and trying to

combine the two would make the paper overwhelming. Indeed this reviewer had 120 comments just about the present content, and s/he is likely to have a similar number for the future papers.

**R1.1** Detailed comments: Abstract: The abstract is pretty long. The first paragraph of the abstract leaves the impression the CV is the solution to the CE/bounce issue of the AMS. This provides a too positive picture of the capabilities of the CV as the second paragraph shows: CE is still not 1.0 for all species; size distributions have lower size resolution; stronger fragmentation is observed and no information about organics is provided – can the AMS still be used to identify different types of organics? I suggest shortening the abstract and providing the most important findings here without overinterpreting the results. It should be avoided to include references in the abstract.

**A1.1** We have shortened the abstract as shown below. The application of the CV to organic aerosols will be addressed in a separate upcoming paper.

**“Aerosol mass spectrometers (AMS) and Aerosol Chemical Speciation Monitors (ACSM) commercialized by Aerodyne are used widely to measure the non-refractory species in submicron particles. With the “standard” vaporizer (SV) that is installed in all commercial instruments to date, the quantification of ambient aerosol mass concentration requires the use of the collection efficiency (CE) to correct for the loss of particles due to bounce on the SV. However, CE depends on aerosol composition and phase thus can vary substantially, leading to additional corrections and/or uncertainty. Although a composition-dependent parameterization of CE in the SV for ambient data has been successfully, CE still contributes most of the estimated uncertainty to reported concentrations, especially in laboratory studies. A new “capture” vaporizer (CV) has been designed to reduce or eliminate the need for a CE correction. CE~1 with the CV for inorganic species in the field has recently been demonstrated.**

**Two high-resolution AMS instruments, one with a SV and one with a CV were operated side by side in the laboratory. Four standard species  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{Cl}$ , which typically constitute the majority of the mass of ambient submicron inorganic species, are studied. The effect of vaporizer temperature ( $T_v$ , 200-800 °C) on the detected fragments, CE and size distributions are investigated. A  $T_v$  of 500-550 °C for the CV is recommended. In the CV, CE was identical (around unity) for more volatile species (e.g.  $\text{NH}_4\text{NO}_3$ ) and**

comparable or higher than the SV for less volatile species (e.g.  $(\text{NH}_4)_2\text{SO}_4$ ), demonstrating an improvement in CE for laboratory inorganic species in the CV. The detected relative intensities of fragments of  $\text{NO}_3$  and  $\text{SO}_4$  species observed with the CV are different than those observed with the SV, and are consistent with additional thermal decomposition arising from the increased residence time and multiple collisions. Increased residence times within the CV also lead to broadened particle size distribution measurements than with the SV. A method for estimating whether pure species will be detected in AMS sizing mode is proposed. Production of  $\text{CO}_2(\text{g})$  from sampled nitrate on the vaporizer surface, which has been reported for the SV, is negligible for the CV for  $\text{NH}_4\text{NO}_3$  and comparable to the SV for  $\text{NaNO}_3$ . We observe an extremely consistent fragmentation for ammonium, compared to very large changes for the associated anions. Together with other evidence, this indicates that it is unlikely that a major fraction of inorganic species vaporize as intact salts in the AMS.”

**R1.2** L18: This sounds as if CE is a function of measurement location, air mass, or season. It could also vary with time of the day, ambient temperature, and other external factors. At the end, CE depends on particle composition and humidity.

**A1.2:** We have revised this sentence per the reviewer’s suggestion:

**“However, CE depends on aerosol composition and phase thus can vary substantially, leading to additional corrections and/or uncertainty.”**

**R1.3** L22: Particle bounce is not “eliminated” as stated here. Particles still bounce off the vaporizer surface however, they are directed into a cavity and have more chances to interact with the vaporizer and to vaporize.

**A1.3:** We have revised this sentence for clarity to :

**“A new “capture” vaporizer (CV) has been designed to reduce or eliminate the need for a bounce-related CE correction.”**

**R.1.4** L35/36: Since the influence of the CV onto ambient size distributions and also onto organic particles was not studied in this work about this no speculations should be made in the abstract and presented as if this were results.

**A1.4:** We agree with the reviewer’s comment, thus have deleted the sentence “**The degradation of CV size distributions due to this broadening is significant for laboratory studies using monodisperse particles, but probably minor for field studies since ambient distributions are typically quite broad**”

We note that the impact of the CV in the measurements of ambient inorganic size distributions has been documented in the following published paper, which was submitted after the present one but moved through the review process faster:

“Hu, W., Campuzano-Jost, P., Day, D. A., Croteau, P., Canagaratna, M. R., Jayne, J. T., et al. (2017). Evaluation of the new capture vaporizer for aerosol mass spectrometers (AMS) through field studies of inorganic species, *Aerosol Sci Tech*, 10.1080/02786826.2017.1296104”

**R1.5** L49: The term “aerosol mass spectrometers” is not a synonym for the Aerodyne AMS as suggested here.

**A1.5:** We have added “**Aerodyne**” before “**aerosol mass spectrometers**”

**R1.6** L85: What is the “differential mobility analyzer (DMA)-impactor technique”? – Explain.

**A1.6:** We have revised this sentence to be:

“**Using the differential mobility analyzer (DMA) coupled to an impactor to quantify the particle bounce fraction,...**”

**R1.7** L86: What do you mean with different “vaporizer surfaces”?

**A1.7:** We have clarified this word to be “**vaporizer porosities**”

**R1.8** L93: Shouldn’t “Aerodyne” be “Aerodyne Res., Inc.”? The reference (Jayne and Worsnop, 2016) is unclear.

**A1.8:** Thanks for reviewer’s suggestion. We have changed the “Aerodyne” to be “Aerodyne Res., Inc.” in this instance, but use “Aerodyne” elsewhere for brevity.

The reference has been revised to clarify that it is a patent: **“Jayne, J. T., and Worsnop, D. R.: Particle capture device, Aerodyne Research, Inc. , US patent 20150040689 A1, 2015.”**

**R1.9** L98: Add “as” after “distributions”.

**A1.9:** Added

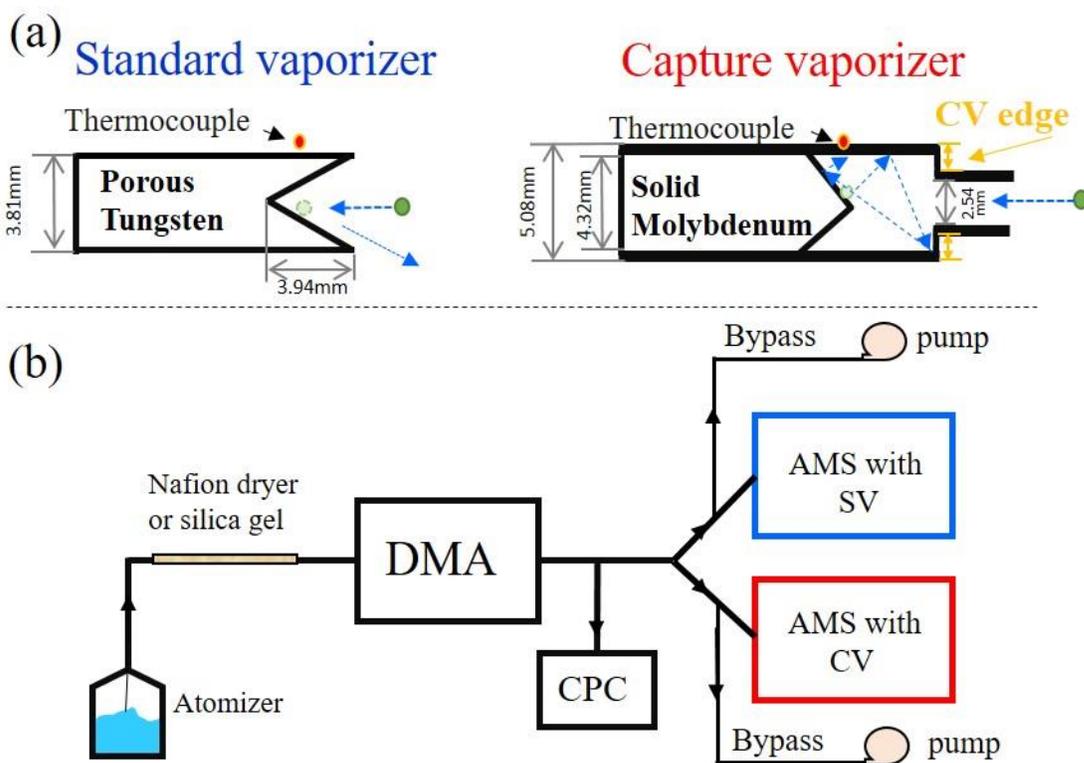
R1.10 L103: “production of CO<sub>2</sub> in the vaporizer while sampling nitrate” – without the information that this CO<sub>2</sub> is from previous deposits this sentence does not make sense to the readers.

**A1.10:** We have added corresponding background before this sentence:

**“Pieber et al. (2016) recently showed that inorganic salts can produce CO<sub>2</sub>(g) from material that is accumulated on the surface of the AMS in the SV, and we investigate whether this effect is observed for the CV.”**

**R1.11** L105: For the measurements presented here (e.g. alignment/misalignment of the particlebeam, size distribution measurements) it would be good to have some information on the dimensions of the CV.

**A1.11:** We have added key dimensions for the SV and CV in Fig. 1(a).



**R1.12** L117: According to Fig. 1 a Nafion dryer or a silica gel dryer were used.

**A1.12:** The text has been modified as follows to address this point:

**“Atomized particles were dried with a Nafion (MD-110-24S-4, Perma Pure LCC, US) or a silica gel diffusion dryer (RH < 30%)”**

**R1.13** L119-121: The authors state that multiply-charged particles were removed using the inlet impactor of the TSI DMA. According to the TSI 3080 manual, different impactor nozzles are used for different flow rate ranges. However, no information on impactor cut-off at certain flow rates is provided. Where are the cut-off diameters for these impactor nozzles and how well do they remove the multiply charged particles? I assume that there is no perfect removal of all multiply charged particles using these impactor nozzles. How large is the uncertainty due to the remaining particles? According to the TSI 3080 manual all three nozzle diameters provided in the text are wrong (should be 0.071 cm instead of 0.0701 cm; 0.0508 cm instead of 0.0580 cm; 0.0457 cm instead of 0.0485 cm).

**A1.13:** We apologize for mislabeling the size of the impactor nozzles. Those values have been corrected in the revised manuscript. Those nozzles were used for with a flow rate between 0.6-0.75 l min<sup>-1</sup>, which are well within the range recommended by TSI manual. The cut-off size was taken from the TSI Aerosol Instrument Manager (AIM, v9.0) software for the exact flow conditions used. The fraction of doubly charged particles can be seen in the size distribution of inorganic species from SV, as shown in Figure 12 . This graph shows a negligible doubly charged mass fraction for NH<sub>4</sub>NO<sub>3</sub> particles and a less than 10% mass fraction for NaNO<sub>3</sub> particles. We have revised our manuscript based on the reviewer’s comment as:

**“To remove multiply-charged particles (required for accurate quantification), impactors with different sizes (i.e. 0.071cm, 0.0508 cm or 0.0457 cm for 0.6-0.75 l min<sup>-1</sup> aerosol sampling flow) were used upstream of the DMA. The particle cut sizes of those impactors varied with flow rate and particle properties, and were taken from the Aerosol Instrument Manager (AIM, v9.0) software from TSI. The mass-based size distributions from SV suggested the doubly-charged particle mass fractions are less than 10% in all cases (section 3.3 Fig. 12-13).”**

**R1.14** L135-137: Did all instruments used for these experiments have the same chamber length?

**A1.14:** Yes, we have added this information in the main manuscript: **“All HR-ToF instruments used for these experiments have the same chamber length (chopper to vaporizer distance: 295 mm), while the Q-AMS had a longer chamber (395 mm).”**

**R1.15** L148 (and many others): Terms like “CPC methods” (methods based on CPC measurements), “particle sizes with 90% transmission : : :” (L152, particles of sizes that have 90% transmission : : :), “organic interference at several inorganic ions” (L269, organic interferences at several m/z associated with inorganic ions), “such hysteresis behavior supports that changes : : :” (L329, such hysteresis behavior supports the assumption that changes : : :), “: : : similar to Drewnick et al. (2015)” (L336, : : : similar to observations by Drewnick et al. (2016)), “The measured PToF times represent both the actual (size dependent) particle velocity plus the vaporization and detection process” (L401-402, the PToF times are the sum of particle travel time

and time for vaporization and detection, the measured times cannot represent a velocity plus a process), “At the edge of the CV, all ions : : : while in the center : : :” (L403, When directing the particle beam onto the edge of the CV, all ions : : : while when the beam was directed towards the center : : :), “AMS/CPC ratios” (L458 and many others, the ratio of a mass concentration and a number concentration is not CE but it would have the dimension  $\text{g} \left( \frac{\text{g}/\text{m}^3}{1/\text{cm}^3} \right)$ , it should be something like the ratio of AMS/CPC-derived mass concentrations), “several secs” (L489, several seconds) are rather laboratory slang than adequate wording of a scientific publication.

**A1.15:** We sincerely appreciate the reviewer’s effort to help improve the clarity of the manuscript. We have changed all the terms reported by the reviewer, where he indicated as well as elsewhere in the manuscript. Particularly for “**AMS/CPC ratios**”, we have changed it to be “**AMS/CPC mass ratios**” in multiple places later on, and defined this term at the first time when it appears in the manuscript:

**“The ratio of the mass concentrations of monodisperse particles as calculated for the AMS (using  $CE = 1$ ) and CPC-derived mass concentrations (hereinafter referred to “AMS/CPC mass ratio”) are shown in Fig. 9 as a function of  $T_v$ .”**

**R 1.16** L151 (and many others): Consistently “evaporation” is used in this text to describe the phase transformation on the vaporizers. “evaporation” is a phase transformation from the liquid into the vapor phase that occurs at a temperature below the boiling temperature at the respective pressure. This is definitely not what happens on the vaporizer. Therefore, “vaporization” should be used throughout the text.

**A1.16:** Thanks for reviewer’s suggestion. We have changed all the “**evaporation**” to be “**vaporization**” or “**evaporate**” to be “**vaporize**”.

**R1.17** L155: Replace “event” by “events”.

**A1.17:** Revised.

**R1.18** L171-173: Is there any information or estimate about the temperature distribution in the CV or about the temperature of the front end of the CV?

**A1.18:** Unfortunately, no such information has been recorded, to our knowledge

**R1.19** L173: Shouldn't be "outside out" rather "outside of"?

**A1.19:** Revised

**R1.20** L180: What exactly means "starts to broaden", how is this start of the broadening of the size distribution defined? How large is the uncertainty of this definition and how large is the uncertainty of a partially detached thermocouple?

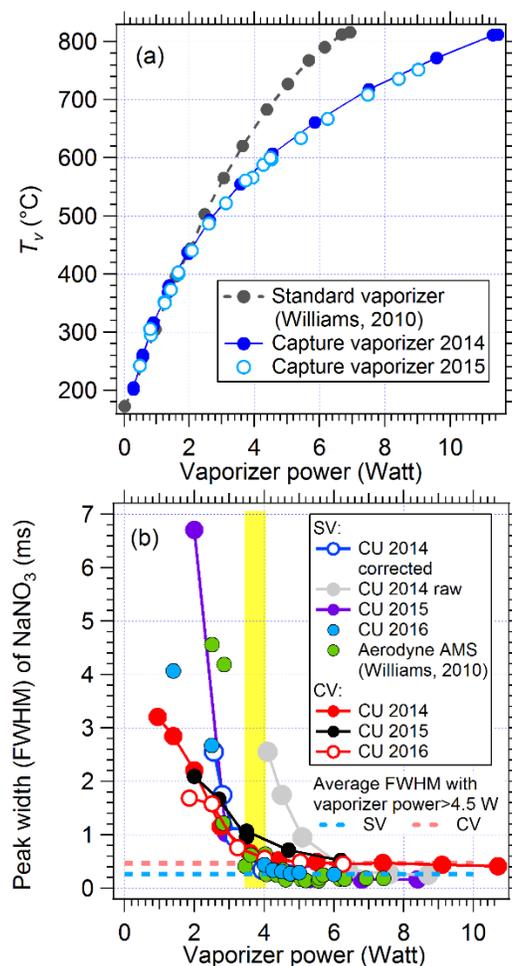
**A1.20:** We have added one sentence to define this broadening:

**"The  $T_v$  of broadening is defined as the temperature at which the size distribution width increases above 20% of the lowest peak width, which was determined by averaging peak width values when vaporizer power is above 4.5 W."**

The uncertainty on the power broadening can be estimated as 1 W, as shown in the updated Fig. 2 below. Since the difference of 1W for vaporizer temperature is around 50 °C we estimate an uncertainty of 50 °C to the  $T_v$  estimation by this method. We have revised the main text to be:

**"Williams (2010) reported that the measured size distribution width (quantified as the full width at half maximum, FWHM) of the NO<sub>3</sub> signal from monodisperse NaNO<sub>3</sub> particles starts to broaden at  $T_v$  below 600°C ( $\pm 50^\circ\text{C}$ ) for SV"**

In our experience, the  $T_v$  error for a detached thermocouple can vary widely, rendering the absolute measurement of little use. It can still be useful in terms of indicating that  $T_v$  has reached a constant value after instrument startup or after at  $T_v$  setting change.



**FIG. 2 (a) Relationship between vaporizer temperature ( $T_v$ , as reported by the attached thermocouple) and vaporizer power. (b) Peak width of measured size distributions of 300 nm  $\text{NaNO}_3$  particles as a function of vaporizer power. In Fig. 2b, the 2014 curve raw (grey trace) between peak width vs vaporizer power in the SV indicated that the vaporizer power reading in that AMS system was inaccurate during those tests (see main text). Therefore, a correction (*Corrected vaporizer power = 0.6 × displayed vaporizer power + 0.1*), which was obtained by matching the CU 2014 curve to the others from SV, was applied. The yellow background shows the range of vaporizer power between 3.6-4 W, where a transition in the detected peak width occurs in both vaporizers. The blue and pink dashed lines are the average values of peak width from CU 2016 curves of the SV and CV (respectively) when vaporizer power is above 4.5 W.**

**R1.21** L189-191: How can the temperature readout deliver power to the vaporizer? This sentence does not make sense for me.

**A1.21:** The AMS EBOX does provide power readout while also supplying the heating voltage and bias to the vaporizer. Due to a change in the overall resistance of the control circuitry, the power readout was no longer properly calibrated. We have clarified this in the revised sentence:

**“It was found that the AMS electronics box (“AMS EBox”) at that time was delivering less power to vaporizer than the readout indicated.”**

**R1.22** L203-207: A “Jayne shape factor” of 0.8 was applied to  $\text{NH}_4\text{NO}_3$  to correct for the fact that the effective density of these particles is less than the bulk density. Is there any explanation why the effective density of ammonium nitrate particles, which are assumed to be liquid and thus droplets, is less than the bulk density? If there is a difference in the effective density and the bulk density for the  $\text{NH}_4\text{NO}_3$  particles, this could also be the case for the other substances. How large is a potential bias or the uncertainty of the results due to this?

**A1.22:** The  $\text{NH}_4\text{NO}_3$  particles are expected to be solid in the vacuum chamber of the AMS ( $<10^{-3}$  mbar). The fact that ammonium nitrate particles have a lower effective density than the bulk density has been documented in several prior studies (e.g. DeCarlo et al., 2004). Further investigation of this topic would necessitate different techniques than those used in this paper, such as e.g. an aerosol mass analyzer and/or atomic force microscopy, which our group does not own, and is out of the scope of this already long paper. We agree that further investigation of this topic would be useful, and have added the following sentence to the paper:

**“Possible reasons for this lower effective than bulk density include particle non-sphericity or the formation of a phase of lower density for the aerosols compared to macroscopic  $\text{NH}_4\text{NO}_3$  (DeCarlo et al., 2004). Experimental investigation of the fundamental reasons for the lower effective density of  $\text{NH}_4\text{NO}_3$  compared to the bulk species is recommended.”**

For the experimental results in this paper, we have estimated the uncertainty of our calculated CE by assigning different uncertainties to SMPS and AMS related measurement. Details can be found in the response A1.71.

**R1.23** L210: I find this section rather long for the information conveyed.

**A1.23** Section 3.1.1 on the comparisons of nitrate and sulfate fragmentation patterns is very important in terms of documenting the performance of CV, and it is necessary to address it in sufficient detail. In addition the  $\text{NO}_x^+$  and  $\text{H}_y\text{SO}_x^+$  ion ratios are used for separating organic/inorganic nitrates (as well as sulfates) using AMS measurement, which has been successfully applied to the field studies (Farmer et al., 2010; Fry et al., 2013; Xu et al., 2015; Hu et al., 2017b). Those fragment ratios are also useful for understanding the  $\text{CO}_2^+$  production artifact in the AMS (Pieber et al., 2016).

**R1.24** L216: Is Figure 3 really necessary? There is a very large number of figures in this manuscript and it would be desirable to reduce this number.

**A1.24:** Yes, we believe this graph is necessary. This figure clearly documents the comparison of the detected fragments of nitrate and sulfate at 70 eV in AMS vs in NIST. Better understanding the fragmentation pattern is crucial for separation of inorganic/organic components and the  $\text{CO}_2^+$  artifact discussed later, see also response A1.23.

**R1.25** L236: Replace “increased collisions” with “increased number of collisions”.

**A1.25:** Revised

**R1.26** L247: Here, for comparison ion ratios for “standard EI” are mentioned. This is a bit confusing/misleading since not the ionization process (EI) is different in the AMS but the vaporization is different and occurs at higher temperatures.

**A1.26:** We agree that this text could be confusing, Thus we have changed “standard EI” to **“the NIST EI database”**

And we have changed the sentence in L248 to read:

**“Given that the ionization process is the same in the AMS vs NIST, the much lower ratios of  $\text{SO}_3^+$ ,  $\text{HSO}_3^+$  and  $\text{H}_2\text{SO}_4^+$  vs  $\text{SO}^+$  from  $(\text{NH}_4)_2\text{SO}_4$  (0.11-0.38) in the SV are indicative of substantial thermal decomposition occurring in the SV, which is even larger in the CV.”**

**R1.27** L255: I suggest replacing “also” with “therefore”.

**A1.27:** Revised

**R1.28** L261-262: Is there any explanation why RIE(SO<sub>4</sub>) is larger for the CV compared to the SV?

**A1.28:** The RIE of sulfate in the CV is not always higher than that in the SV. A wide range of sulfate RIE in the HR-ToF-AMS with CV (1.3-2.4) has been measured by combining this and other unpublished studies. It suggests the RIE of sulfate in CV-AMS is comparable or higher than those in the SV (typically in the range of 1.1-1.4). A sulfate RIE of 1.1 was observed for the CV in ACSM (Hu et al., 2017). Sulfate RIE can be influenced by many aspects including detailed ionizer, vaporizer, and filament positions, ion optics tuning etc. One possibility for higher sulfate RIE observed in this is the differences of decay and rise time of sulfate between the SV and CV. For nitrate, fast decay of nitrate in NH<sub>4</sub>NO<sub>3</sub> ( $\tau < 1$ s) was observed in both SV and CV under  $T_v = 500$ - $600$  °C, as shown in Fig. 10. However, a faster SO<sub>4</sub> decay and arise signal in the CV ( $\tau < 2$ s) than in the SV ( $\tau \sim 13$ s) was found (Fig.11), which could result in a relative higher differential sulfate/nitrate signal ratios in the CV than SV within the time interval of MS mode ( $\sim 5$ - $6$ s). To clarify these points, we have revised this text as:

**“RIE<sub>SO4</sub> ~1.2 was found in the SV in this study, the same as the default value in the AMS analysis software. RIE<sub>SO4</sub> measured with the CV in this study was ~1.7-2.4, although values as low as 1.1 have been observed in the CV with ACSM (Hu et al., 2017a). Sulfate RIE can be influenced by many aspects including detailed ionizer, vaporizer, filament positions and turning of ion optics. Differences in the timescales on which sulfate particles fully vaporize on the SV and CV, as discussed in section 3.2, could also give rise to differences in the measured RIE<sub>SO4</sub> for different vaporizer.”**

**R1.29** L265: I suggest replacing “recommended fragmentation table” with “recommended changes of the fragmentation table” since only the changes are presented in Table1, not the whole fragmentation table.

**A1.29:** Changed

**R1.30** L269: Here it is stated that “the fragmentation of organics is also different in the CV”. This was not shown in the experiments presented in this manuscript and is not published. If this is an assumption this should be made clear.

**A1.30:** These organic results are extensive, and will be shown in a separate upcoming paper. We have removed this sentence.

**R1.31** L285-287: The statement that for the CV the  $\text{NO}_2^+/\text{NO}^+$  ratio showed less dependence on temperature than for the SV is not correct. According to the numbers provided here, the ratio changes by 62.5% for the CV while it changes by 40% only for the SV. So the dependence is even larger for the CV than for the SV.

**A1.31:** We have revised this sentence to read:

**“For the CV,  $\text{NO}_2^+/\text{NO}^+$  varied within a small range as  $T_v$  changed, and was an order of magnitude lower (0.015-0.04) than the SV, as discussed above.”**

**R1.32** L291-293: The boiling points are relevant for ambient pressure only; under the conditions on the vaporizer boiling will start at much lower temperatures. May be this should be mentioned here. “substantially are higher” should be replaced with “substantially higher”. “In SV : : :” should be replaced with “In the SV : : :”.

**A1.32:** We have added one sentence to remind the reader of this fact. We also have revised the grammar as the reviewer suggested:

**“ $\text{NaNO}_3$  is less volatile than  $\text{NH}_4\text{NO}_3$  with melting and boiling points of 306 and 380°C respectively, substantially higher than for  $\text{NH}_4\text{NO}_3$  (melting point of 169°C and boiling point of ~210°C; Haynes, 2015). Since boiling points are referenced to 1 atm, these species will boil at lower temperatures under the vacuum of the AMS vaporizer. Here we are using the boiling points as indicators of relative volatility of different species.”**

**R1.33** L299-301: Also here it is claimed that the  $\text{NO}_2^+/\text{NO}^+$  ratios show less dependence on  $T_v$  for the CV than for the SV. While it is true that the values of this ratio are much lower for the CV than for the SV, the change with changing  $T_v$  is a factor of 20 for the SV while it is a factor of 60

for the CV. So the dependence on  $T_v$  is also in this case larger for the CV than for the SV, contrary to what is claimed in the text. In addition, the numbers provided in the text for the ratios observed for the SV (0.01-0.03) do not agree with the data presented in Figure 4b (rather 0.005 – 0.095).

**A1.33:** We have revised this sentence per the reviewer’s suggestion and corrected the stated range of values:

**“In the CV, much lower  $\text{NO}_2^+/\text{NO}^+$  ratios for  $\text{NaNO}_3$  (0.001-0.006) were observed compared to those from the SV (0.005-0.1), consistent with the results for  $\text{NH}_4\text{NO}_3$ .”**

**R1.34** L305: Here, it should be stated what is thermally decomposed to avoid confusion.

**A1.34:** Corresponding information has been added:

**“As  $T_v$  increased, the relative abundance of the heavier ions ( $\text{HSO}_3^+$  and  $\text{SO}_3^+$ ) decreased and  $\text{SO}_2^+$  increased, consistent with increasing thermal decomposition of  $(\text{NH}_4)_2\text{SO}_4$  with more abundant  $\text{SO}_2(\text{g})$  and lower  $\text{H}_2\text{SO}_4(\text{g})$  in the thermal decomposition products”**

**R1.35** L306-307: From Figure 4c it does not look like that there is a change in  $\text{SO}_x^+/\text{SO}^+$  ratios for  $T_v < 300\text{C}$  only and then the ratio levels off, as stated in the text. It rather looks like that for higher  $T_v$  the  $\text{SO}_2/\text{SO}$  ratio decreases again and the  $\text{SO}_3/\text{SO}$  ratio seems to increase.

**A1.35:** In general, we cannot discuss every small variation in every graph in the main text, as it would make the manuscript very long and difficult to read. In the interest of brevity, we are focusing on and describing the largest variations of the plotted quantities, but the graphs themselves allow examining finer details for anyone interested. In this case, here we tried to describe the big picture of  $\text{SO}_x^+/\text{SO}^+$  trend. The changes at higher vaporizer temperatures ( $>700\text{C}$ ) are small ( $<20\%$ ) And the  $\text{SO}_3^+/\text{SO}^+$  and  $\text{HSO}_3^+/\text{SO}^+$  ratios do not show a clear trend with temperature increasing above  $600\text{C}$ . Thus, we have kept the original description in the manuscript here.

**R1.36** L319: Replace “particle” with “particles”.

**A1.36:** Revised.

**R1.37** L320: Remove the first “from”.

**A1.37:** Revised.

**R1.38** L323-325: It is unclear to me how the variations in the Cl/HCl ratio are due to the stickiness of HCl on the vaporizer surface.

**A1.38:** We have clarified this sentence to be:

**“The small variations of  $\text{Cl}^+/\text{HCl}^+$  vs  $T_v$  may have been due to the changing background of  $\text{Cl}^+$  and  $\text{HCl}^+$  due to the different stickiness of chloride decomposition products on the vaporizer surface and ionization chamber walls.”**

**R1.39** L332-333: Replace “vaporization surfaces” with “vaporizer surfaces”.

**A1.39:** Revised

**R1.40** L356: Replace “: : : pure  $\text{NH}_4\text{NO}_3$  since : : :” with “: : : pure  $\text{NH}_4\text{NO}_3$  particles since : : :”

**A1.40:** Added

**R1.41** L360: I suggest replacing “movement” with “experiment”.

**A1.41:** Changed

**R1.42** L363-364: Replace “: : : cross section of vaporizer : : :” with “: : : cross section of the vaporizer : : :” and “vertical directions” with “vertical movements”.

**A1.42:** Revised.

**R1.43** L371: Move “( $\_0.07$ )” after “low  $\text{NO}_2^+/\text{NO}^+$ ”.

**A1.43:** Revised.

**R1.44** L373: There are several data points in Figure 6 which show  $\text{NO}_2^+/\text{NO}^+$  ratios for the SV below the range provided here (0.29-0.75). These low values could be associated with very low signal intensities, therefore error bars or a discussion of the uncertainties is necessary.

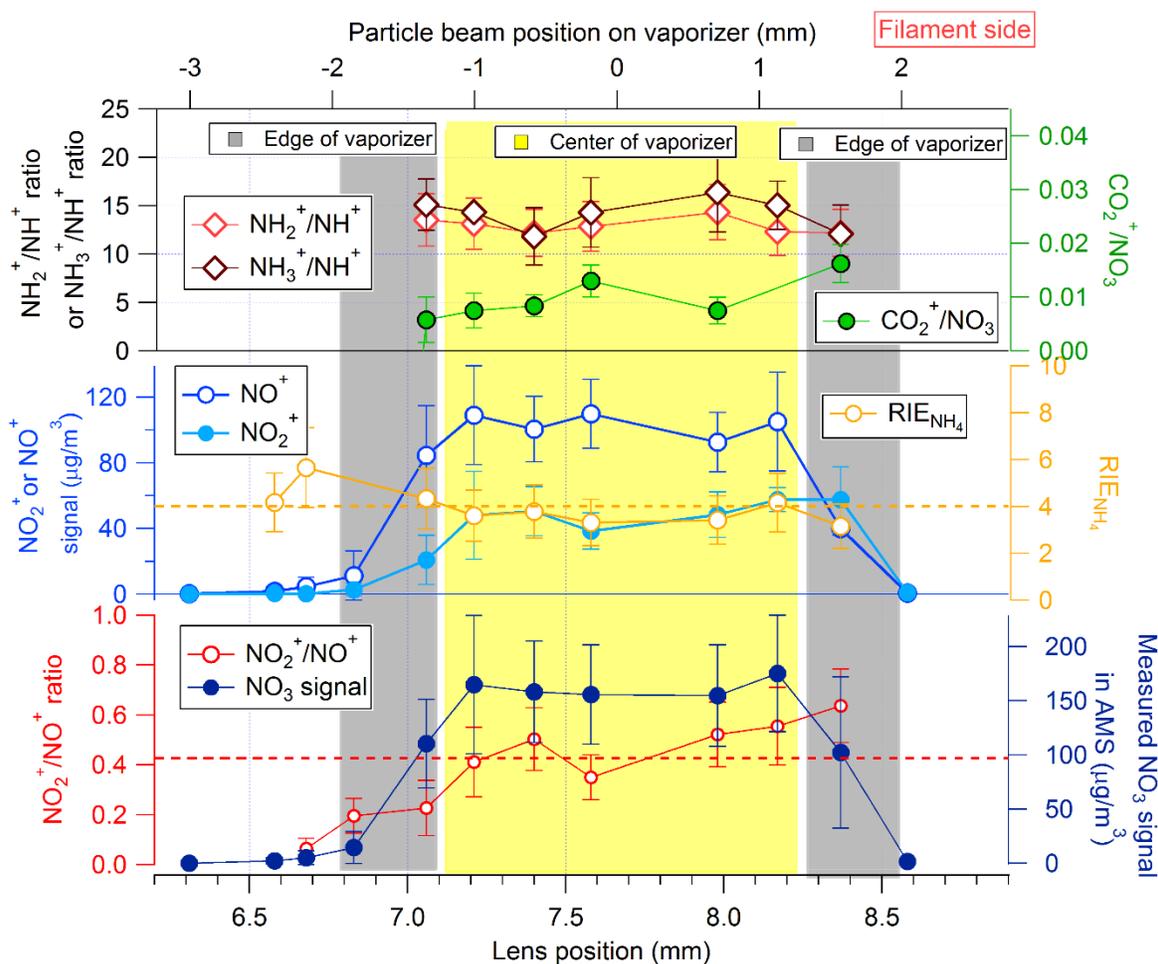
**A1.44:** First, as stated in the manuscript, this experiment was done in a Q-AMS. We have added the following text to the figure caption to clarify this point.

**“This experiment was performed in a Q-AMS, due to limitations of instrument availability, and led to lower signal-to-noise ratios than when using a ToF-AMS, which was used for the rest of this manuscript”**

Second, we have clarified that the values quoted are those observed for the  $\text{NO}_2^+/\text{NO}^+$  ratio in the center of the SV, which removes the confusion with the low values sometimes observed on the edges of the SV:

**“Those values are similar to those observed for the center of the SV (0.29-0.75)”**

Per the reviewer’s suggestion, we have added variability bars to the graph. The error bar is the standard deviation. Due to the time limitation for the experiment sometimes only 1 data point was acquired for a given position. The variability of those single points were estimated by averaging those from neighboring positions. It is reasonable to find higher signal variability in the Q-AMS<sub>sv</sub> than HR-ToF-AMS<sub>cv</sub>. The  $\text{NO}_2^+/\text{NO}^+$  points which are out of the vaporizer edge (<6.6 mm) have been removed in Fig.6 due to the very large uncertainties associated with very low signal intensities there. The updated Fig. 6 is reproduced below.



**FIG. 6 SV: particle beam position dependence of  $\text{NO}_2^+/\text{NO}^+$ , total nitrate,  $\text{NO}_2^+$  and  $\text{NO}^+$  signals, RIE of  $\text{NH}_4$ ,  $\text{NH}_2^+/\text{NH}^+$ ,  $\text{NH}_3^+/\text{NH}^+$  and nitrate equivalent mass ratio of  $\text{CO}_2^+/\text{NO}_3$ . The shaded areas are a rough indication for where the particle beam hits the vaporizer. A constant IE obtained with pure  $\text{NH}_4\text{NO}_3$  particles at the center of the lens was applied to all data collected in this experiment. The error bars represent the measurement variability the standard deviation of each point. If only one data point for one position was obtained, the error bar for that point was estimated by averaging those from nearby positions. The particle size-resolved detection for the edge and center positions are shown in Fig. 7. This experiment was performed in a Q-AMS, due to limitations in instrument availability, and led to lower signal-to-noise ratios than when using a ToF-AMS, which was used for the rest of this manuscript.**

**R1.45** L375: “: : : when the particle beam hits the CV edge, as illustrated in Fig. 1a.” This is not illustrated in Figure 1a.

**A1.45:** We have revised the sentence to clarify:

**“... when the particle beam hits the CV edge. The edge position is illustrated in the Fig. 1a.”**

**R1.46** L379-386: As a potential reason for higher NO<sub>3</sub> signal when the particle beam is directed towards the edge of the CV, reduced fragmentation and higher HNO<sub>3</sub>(g) fraction is mentioned. Another possible reason could be lower vapor molecule velocity due to the lower temperature at the front end of the CV and consequently longer residence time of the molecules in the electron beam.

**A1.46:** Thanks for the reviewer’s suggestion. This potential explanation has been added to the text:

**“The slightly higher NO<sub>3</sub> signal on the edge of CV may be due to (1) a higher IE<sub>NO<sub>3</sub></sub> resulted from the different spatial distribution of vapor molecules, which may better overlap the electron beam and/or ion extraction regions, (2) or higher IE<sub>NO<sub>3</sub></sub> due to longer residence time of the molecules in the electron beam, due to the lower vapor molecule velocity resulting from the lower temperature at the front end of the CV, (3) or a different RIE of the particle vapor resulting from a change in thermal decomposition products on the vaporizer.”**

**R1.47** L386: “: : : on the right edge vs left edge : : :” should read “: : : on the left edge vs right edge : : :”

**A1.47:** Corrected.

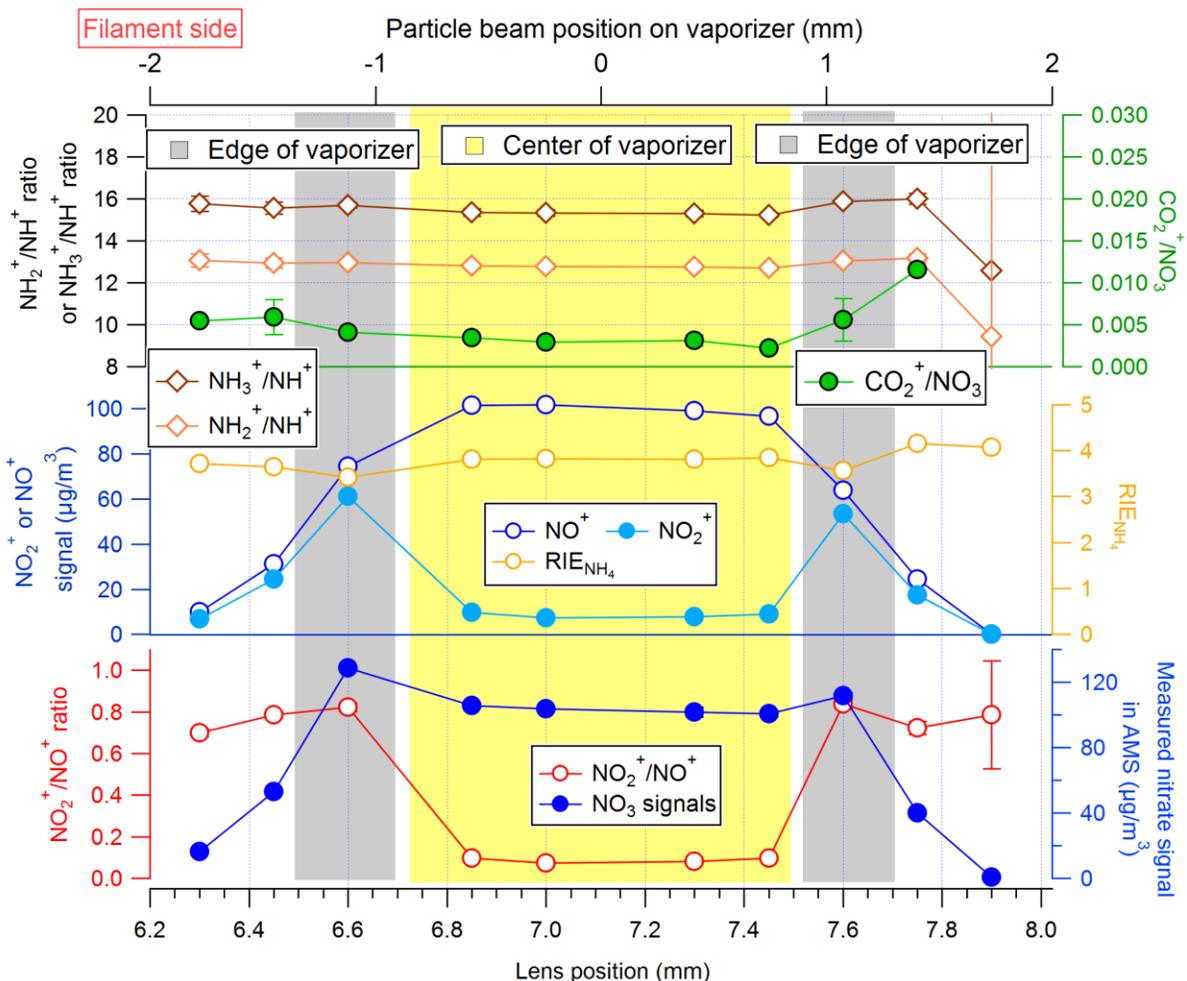
**R1.48** RL390-391: Here it is claimed that in the SV no enhanced nitrate signal was observed on the vaporizer edge. When looking at Figure 6 it looks like there is a small enhancement of nitrate signal at both edges of the vaporizer. However, without error bars it is hard to judge whether this is significant.

**A1.48:** The uncertainties of measured  $\text{NO}_3$  mass have been added to the revised Figure 6, as discussed and shown in response A1.44. Those enhancements of nitrate signals are within the variability of other measured nitrate signals in the center position. And most importantly, those small enhancements occur still within the central region of the vaporizer. If the enhanced points were at the edge of vaporizer, the vaporizer diameter would be less than 2 mm, which is much smaller than the real diameter (should be 3.81 mm, as shown in the updated Fig. 1 in response A1.11).

**R1.49** L390-393: While here, differences in  $\text{NO}_2^+/\text{NO}^+$  ratio between SV vaporizer center and edge are discussed, the clear trend of this ratio across the vaporizer is not discussed. What is the reason for this trend?

**A1.49:** We do not know the exact reason of this increasing trend. For reference, we have added the filament position in Fig. 5, which might be related to this trend (See updated Fig. 5 below) and Fig. 6 (see updated Fig. 6 in response A1.44). The following sentence has been added to main text to address this point:

**“The reason for the slightly increasing trend of  $\text{NO}_2^+/\text{NO}^+$  ratios toward the filament side in Fig.6 is unclear.”**



**FIG. 5 CV: Particle beam position dependence of  $\text{NO}_2^+/\text{NO}^+$ , total detected nitrate,  $\text{NO}_2^+$  and  $\text{NO}^+$  signals,  $\text{RIE}_{\text{NH}_4}$ ,  $\text{NH}_2^+/\text{NH}^+$ ,  $\text{NH}_3^+/\text{NH}^+$  and nitrate equivalent mass ratio of  $\text{CO}_2^+/\text{NO}_3$ . The shaded areas are a rough indication for where the particle beam hits the vaporizer. A constant IE obtained with pure  $\text{NH}_4\text{NO}_3$  particles at the center of the lens was applied to all data collected in this experiment. The error bars are the variabilities (standard deviation) for each point. Some error bars cannot be seen in this figure is because their values are very small. The particle size-resolved detection for the edge and center positions are shown in Fig. 7.**

**R1.50** L396-397: “Slightly lower  $\text{RIE}(\text{NH}_4)$  are observed at the edges of the CV due to higher nitrate signal and constant  $\text{NH}_4$  signal.” The higher nitrate signal and constant  $\text{NH}_4$  signal is not

the reason for the lower RIE for ammonium (as suggested by this sentence) – this is just the observation. What is the reason?

**A1.50** We do not know the exact fundamental reason behind this trend. As in R1.49 and some other questions, the information collected with the AMS can be insufficient to definitely characterize the reasons behind every trend in every single parameter measured. We have revised the sentences as below:

**“Slightly lower  $RIE_{NH_4}$  are observed at the edges of the CV, which might be due to changes in the mix of vapor species formed from nitrate ( $HNO_3(g)$ ,  $NO_2(g)$  and  $NO(g)$ ) while the vapor formed from  $NH_4$  stays the same ( $NH_3(g)$ ).”**

**R1.51** L397-398: The authors claim that there is no systematic difference of  $RIE(NH_4)$  between center and edges. If I compare Figure 5 and Figure 6 I would say that the dip of  $RIE(NH_4)$  at the edge of the CV (Figure 5), which was claimed to be real, is of similar magnitude as the trend of  $RIE(NH_4)$  across the SV (Figure 6). Without a proper discussion of the uncertainties all this is highly subjective.

**A1.51:** The uncertainties have been added to Figure 6, as discussed and shown in response A1.44. The uncertainty of  $RIE_{NH_4}$  is much higher in the Q-AMS<sub>SV</sub> than ToF-AMS<sub>CV</sub> due to the low signal to noise of  $NH_4NO_3$  measured in the former instrument. The manuscript has been revised to clarify this point.

**“In the SV, we did not find systematic differences of  $RIE_{NH_4}$  between the center and edges, within their higher uncertainties (Fig. 6).”**

**R1.52** L407: “Fig. 7a” must be “Fig. 7c or d”.

**A1.52:** Revised.

**R1.53** L411-412: Not the measured PToF times are narrow (as written) but the measured PToF time distributions.

**A1.53:** Revised.

**R1.54** L420: Here the authors suggest that for correction of the CO<sub>2</sub> signal that is produced on the surface of the vaporizer the fragmentation table should be adjusted. I doubt that this is possible. As the authors show in their manuscript the CO<sub>2</sub> generated on the surface of the vaporizer depends on the history of the vaporizer (i.e. on the material that was previously deposited on the vaporizer) and thus is potentially highly variable.

**A1.54:** This is not a new finding of our paper, rather it is a summary of the results of the Pieber et al. (2016) study, which we cited at the start of this paragraph. Those authors already showed that this correction method works. The quantitative information for correcting the fragmentation table can be obtained by carrying out experiments on each individual AMS, most importantly the IE calibrations with NH<sub>4</sub>NO<sub>3</sub> that are routinely performed on all AMSs. To clarify, a text revision has been made:

**“This causes an interference in the quantification of organic species, which can be corrected by adjustments to the fragmentation table using experimental results for an individual AMS instrument (e.g. the measured CO<sub>2</sub><sup>+</sup>/NO<sub>3</sub> ratio during IE calibrations with NH<sub>4</sub>NO<sub>3</sub>).”**

**R1.55** L424: Were NH<sub>4</sub>NO<sub>3</sub> particles sampled in air or in argon for these experiments?

**A1.55:** These were sampled in air. However Pieber et al. (2016) showed that the interference was also observed when sampling particles under other gases when O<sub>2</sub> was not present. We refer the reviewer to Pieber et al. (2016) for further details.

**R1.56** L432-437: Two different reasons for negligible CO<sub>2</sub> formation in the CV (compared to the SV) when sampling ammonium nitrate particles are provided: Different thermal decomposition pathways between the vaporizers (mainly NO(g) produced in the CV while in the SV also NO<sub>2</sub>(g) is produced) and different vaporizer materials (molybdenum in the CV which is more inert than tungsten used in the SV). For me the first reason is not very convincing: in the CV, thermal decomposition into NO is the consequence of more interaction of the material with the vaporizer due to the trapping in the cavity. During the first interaction with the vaporizer I would expect that thermal decomposition is similar to that observed on the SV with similar fractions of NO<sub>2</sub>(g) as in the SV. This NO<sub>2</sub> should then result in similar production of CO<sub>2</sub> from material on the vaporizer surface as in the SV.

**A1.56:** We still think the first reason is possible. The reviewer is assuming that in the CV  $\text{NO}_2(\text{g})$  will be an important thermal decomposition product, that will turn into  $\text{NO}(\text{g})$  through successive collisions. If that is the case, then the 2<sup>nd</sup> reason (Mo being less reactive than W for the process leading to  $\text{CO}_2$  formation) will apply. However, it is also possible that a much larger fraction of the initial products from  $\text{NH}_4\text{NO}_3$  in the CV is  $\text{NO}(\text{g})$ , given the different vaporizer materials, which is the 1<sup>st</sup> reason given. Thus, we believe that this text correctly reflects both possibilities.

**R1.57** L437: I suggest replacing “: : : based on lens alignment : : :” with “: : : dependent on lens position : : :”.

**A1.57:** Revised.

**R1.58** L439: The  $\text{CO}_2^+/\text{NO}_3$  ratios are a little higher at the vaporizer edge. Is this difference significant? There is very low signal intensity, likely associated with high uncertainty.

**A1.58:** Based on the uncertainty we calculated in the Fig. 5, we think the slightly higher  $\text{CO}_2^+/\text{NO}_3$  ratios at the edge is robust, since good signal-to-noise levels were obtained there.

**R1.59** L447-449: Here the authors explain the  $\text{CO}_2^+$  artifact in the CV from  $\text{NaNO}_3$  (but not from  $\text{NH}_4\text{NO}_3$ ) by the substantial  $\text{NO}_2(\text{g})$  formation from  $\text{NaNO}_3$ . This is a contradiction to what was shown in section 3.1.2 where the authors show that  $\text{NaNO}_3$  produces much less  $\text{NO}_2$  compared to  $\text{NH}_4\text{NO}_3$ . According to this the  $\text{CO}_2^+$  artifact should behave the opposite way. Also the related statement about  $T_v$  dependence of the  $\text{CO}_2^+$  artifact contradicts the observations in 3.1.2 and Figure 4a/b: also at low  $T_v$  the  $\text{NO}_2^+/\text{NO}^+$  ratio is about 10 times lower for  $\text{NaNO}_3$  compared to  $\text{NH}_4\text{NO}_3$ .

**A1.59:** Our experimental results are consistent with those reported by Pieber et al. (2016), who found an order of magnitude higher  $\text{CO}_2/\text{NO}_3$  ratio with  $\text{NaNO}_3$  particles sampled than  $\text{NH}_4\text{NO}_3$  particles in the SV, while a an order of magnitude lower  $\text{NO}_2^+/\text{NO}^+$  ratio was found in  $\text{NaNO}_3$  than  $\text{NH}_4\text{NO}_3$ . However we agree that there was some contradiction between the passages mentioned by the reviewer. While we could speculate even further about what is going on, we prefer to simplify this text given the lack of firm constraints:

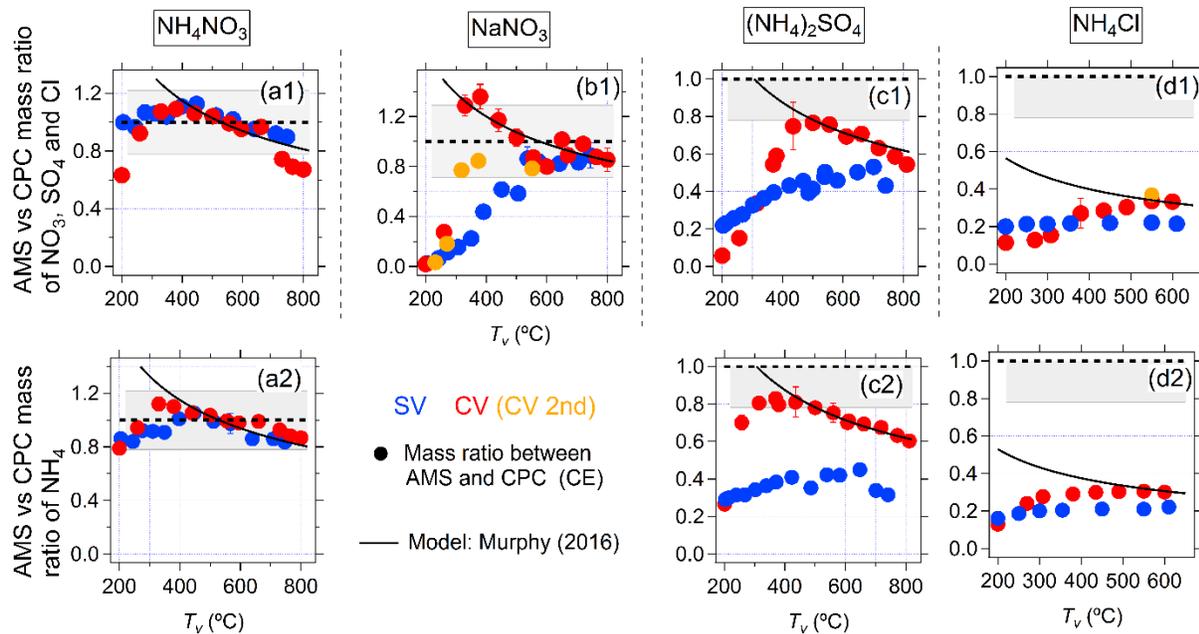
“The fundamental reason for  $\text{CO}_2^+$  artifact in the CV from  $\text{NaNO}_3$  (but not  $\text{NH}_4\text{NO}_3$ ) is not clear. Higher  $\text{CO}_2^+/\text{NO}_3$  ratios when sampling  $\text{NaNO}_3$  particles than with  $\text{NH}_4\text{NO}_3$  particles have also been observed in this (Fig. 8b) and previous studies with SV-AMS (Pieber et al., 2016).”

**R1.60** L453-469: Vaporizer-temperature dependent collection efficiencies for the CV determined by comparing the calculated mass concentrations from CPC measurements with AMS mass concentrations should show a  $\text{SQRT}(\text{Mw})$  dependence as predicted by Murphy (2016) since the vapor molecules emitted from the vaporizer should be in good thermal equilibrium with the vaporizer after leaving the cavity. Was this observed in the measurements?

**A1.60:** Thanks for the reviewer’s suggestion. To investigate this point we made a new figure and added some text to the sup. Info., including a new figure:

### **S1.5. New evidence about the $T_v$ -dependence of signals in the CV-AMS**

According to Eq (2) in Murphy (2016a), and in the absence of other effects, measured signal intensities and timescales should follow  $1/\sqrt{T_v}$  dependence as  $T_v$  is varied. Such a dependence is not observed in SV data, either for single particle timescales of pure species, or for total signal from ambient particles, indicating the importance of other effects neglected in the Murphy model (Jimenez et al., 2016). That may be at least partly due by the fact that vaporization occurs at  $T < T_v$ , due to evaporative cooling (Saleh et al., 2017). This point can now be evaluated for the CV using the AMS/CPC mass ratio data in Fig. 9 (replotted in Fig. S3), since the data is only calibrated with the RIEs determined at  $\sim 600^\circ\text{C}$ . Such a dependence appears to be observed for 3 of the 4 species for part of the temperature profile. This suggests that the Murphy model may be a closer approximation of AMS detection when the CV is used, possibly because important SV processes such as particle bounce onto colder ionizer surfaces are suppressed with the CV. The different dependences observed for the SV in most cases highlight the substantial differences between the SV and CV in detection properties.



**Figure S3** Ratios of mass concentration between AMS and CPC measurements (CE) from four inorganic species (dried monodisperse particles) of (a) 300 nm  $\text{NH}_4\text{NO}_3$ ; (b) 250 nm  $(\text{NH}_4)_2\text{SO}_4$ ; (c) 300 nm  $\text{NaNO}_3$ ; (d) 300 nm  $\text{NH}_4\text{Cl}$ . The black line was calculated based the relationship described in Eq. (2) of Murphy (2016a), which predicts that the measured AMS intensity should follow  $1/\sqrt{T_v}$  dependence as  $T_v$  is varied. The black curves have been arbitrarily scaled vertically to match the red CV point around 600 °C. A dependence for CV consistent with the theory appears to be observed for several species at the higher end of the  $T_v$  profiles. Gray shading represents the estimated uncertainty range (see Fig. 9 in the main text and associated discussion for details).

**R1.61** L465: Why were 300 nm  $\text{NaNO}_3$  particles used for the measurements and a (relatively large) correction factor applied to correct for incomplete lens transmission instead of using 250 nm  $\text{NaNO}_3$  particles? I would expect that this would result in much lower uncertainties in the results.

**A1.61:** A particle size of 300 nm was initially chosen for the CE experiments in this study. At this size, most particles can be fully transmitted through the aerodynamic lens, and the presence of doubly charged particles can be significantly reduced. By using 300 nm  $\text{NaNO}_3$  particles, interferences of less than 10% on mass distribution due to doubly charged particle was observed, as shown in Fig. 12b (also see figure in response A1.13). When we performed  $\text{NaNO}_3$  experiments, we did not realize that the aerodynamic size of  $\text{NaNO}_3$  exceeded the 100% lens transmission range (of an underperforming lens in that particular instrument and time) due to their higher density.

We repeated the experiment to obtain a second trace of  $\text{NaNO}_3$  ( $d_m=300\text{nm}$ ) CE in the CV (orange trace in Fig. 9b1), which shows similar AMS/CPC mass ratios as the first trace. Due to limitations of the experimenter's time and also of instrument availability due to ongoing field studies, we cannot repeat this experiment with a different particle size within the time frame of the responses of this manuscript.

To account for the lens transmission uncertainty, we have calculated the final uncertainties of AMS/CPC mass ratios including the uncertainty of AMS lens transmission loss. The detailed calculation and result are shown in response A1.71

**R1.62** L471: If it is really  $1\pm 0.07$  then you should write “ $1.00\pm 0.07$ ”.

**A1.62:** Revised.

**R1.63** L475: I disagree with the statement that the AMS/CPC nitrate mass ratios for  $\text{NH}_4\text{NO}_3$  did not show a clear trend with  $T_v$  for the SV. According to Figure 9a1 there is also for the SV a clear maximum around 400-450 °C.

**A1.63:** The observed trend is weak, except at the extreme temperatures sampled. However, for simplicity this sentence has been removed.

**R1.64** L479-481: If the smaller AMS/CPC mass ratio for the CV for very low  $T_v$  is due to slow vaporization this should also be the case for the SV where vaporization occurs at the same temperature. However, for the SV no such strong decrease in the ratio is observed for very low  $T_v$ .

**A1.64:** We think this interpretation is reasonable, which can be verified by the signal decay and rise from  $\text{NH}_4\text{NO}_3$  particles when changing chopper positions at 200 °C, as shown in Figure 10. Slower decay and rise of nitrate signal was observed in the CV than SV under 200°C, the reason for which is not clear. However, this slower variation can lead to a lower AMS/CPC mass ratio in the CV within the MS mode timescale (5-6 s) than SV, when using  $\text{IE}_{\text{NO}_3}$  from 600°C at which temperature decay and rise nitrate signals are similarly fast in both vaporizers.

**R1.65** L482-485: Why should the interaction of the analytes with the vaporizer surface be stronger at hot surfaces? I would expect the opposite behavior.

**A1.65:** The reviewer's this comment is similar to the question R1.70. In the original manuscript, we found we have repeated the explanation in the following paragraph with results from beam-open and -closed experiment as well. Thus we deleted this sentence "" here to avoid wordiness in the paper. The detailed response to the reviewer's question can be found in A1.70

**R1.66** L494: How is tau defined? In Drewnick et al. 2015 it was discussed that the decrease or increase of the signal could not be described with a single time constant but the time constants changed over time.

**A1.66:** The definition of Tau was already given in the sentence after line 494 as " **$\tau$  is defined here as the lifetime of signal decay when closing the particle beam after a long period (>several minutes in this study) of exposure to incoming particles. It was estimated through an exponential fit to the relevant part of the signal time series.  $\tau$  for the signal rise after a long period without particles impacting the vaporizer is not shown, since it varies in the same way.**"

We have read through Drewnick et al., 2015 and did not find the exact sentences with the information discussed by the reviewer. We believe what the reviewer points out here is probably about the background cleaning and accumulation for semi-refractory species (e.g. NaCl, FeCl<sub>3</sub>, 6H<sub>2</sub>O etc) shown in Drewnick et al. (2015). Most of the species used in our studies do not fall into this category. Only NH<sub>4</sub>Cl shows some signs of substantial stickiness to the vaporizer/ionizer surfaces. We have added one sentence to remind the reader of the fact that  $\tau$  can change over time for semi-refractory or sticky species.

**"Note that  $\tau$  might change over time for very sticky or semi-refractory species (e.g., NaCl or FeCl<sub>3</sub>) (Drewnick et al., 2015)."**

**R1.67** L498-500: Why is the decay of the nitrate signal faster for the CV than for the SV? Due to the geometry of the two vaporizers the opposite behavior would be expected. What is the uncertainty of these results?

**A1.67:** We are confident on those experimental results, since very repeatable results have been observed. We have added the following text with a tentative explanation:

**“We speculate the scattered particles onto nearby surface of ionization chamber could result a slower decay due to colder chamber surfaces. As the CV inhibits particle bouncing/scattering, this results in faster decay. This clearer separation of processes is one of the advantages of CV than SV.”**

**R1.68** L500-501: The sentence starting with “Slower decays : : :” makes no sense to me.

**A1.68:** To make the text clearer, we have revised this sentence to be:

**“At lower  $T_v$  (200°C) nitrate signal decays to 16% of open signal in the SV after 3 s and to 24% in the CV after 2 s, respectively, showing a slower decay of nitrate signal at lower temperatures.**

**R1.69** L504-505: Here vaporization processes and the residence times in the two vaporizer types are mixed together. It is not slow vaporization which causes the nitrate signal to decay slower in the CV but the times the vapor needs to escape the vaporizers. The vaporization process itself should not have different time constants for the two vaporizer geometries since it occurs at the same temperature.

**A1.69:** It is not clear whether the reviewer is correct here. The temperatures are nominally the same, but they could have some differences in reality, due to different thermocouple locations, and also the existence of some temperature differences at different points in each vaporizer. Also the vaporizer materials being different could lead to some differences. We have revised the sentence to more clearly list both possibilities, while indicating that escape time is the more likely one, as:

**“Thus this experiment indicates that the longer time for the vapors produced from nitrate vapor to escape the CV (and possibly for vaporization) at lower  $T_v$  was the reason for the lower nitrate signal detected in this case.”**

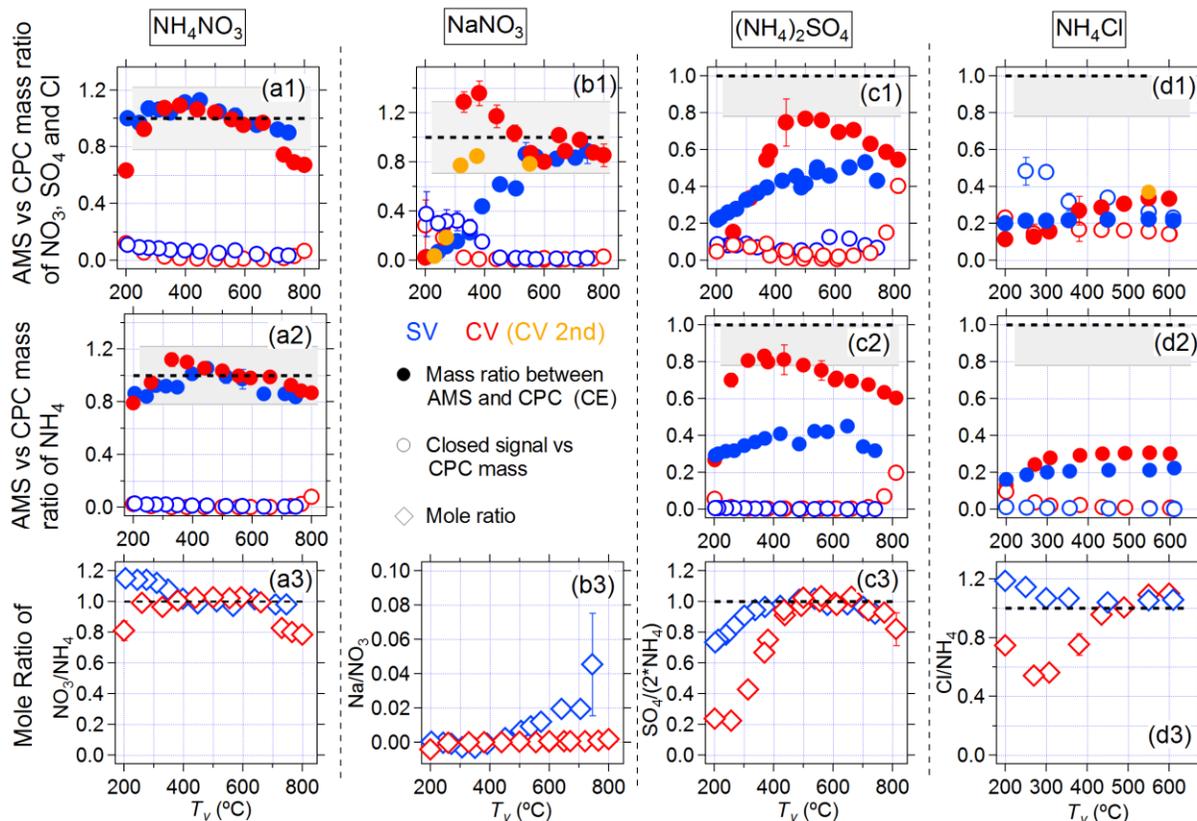
**R1.70** L506-510: I find it counter-intuitive that at higher  $T_v$  stronger interactions between the decomposition products from nitrate and the vaporizer surfaces should occur. I would expect the opposite. Isn't it possible that at higher vaporizer temperatures also the surrounding ionizer cage is hotter resulting in more desorption of material and consequently in larger background signals?

**A1.70:** We agree with reviewer’s suggestion that the desorption of material from the surrounding ionizer cage is a possible explanation. We still think a stronger interaction between thermal decomposition product and vaporizer surfaces are one of the possibilities since we do not know what chemical reactions can happen at high  $T_v$ . Thus, we have revised our manuscript to be:

**“This elevated background signal at higher  $T_v$  ( $> 700^\circ\text{C}$ ) may be due to either of (1) hotter surrounding ionizer cage containing deposited nitrate results in more desorption of nitrate vapors; and/or (2) stronger interactions between the species decomposing from nitrate and the hot vaporizer surfaces.”**

**R1.71** L517: The AMS/CPC mass ratio of 0.85 is the result of several assumptions or corrections (RIE for  $\text{NO}_3$  from  $\text{NaNO}_3$ , Jayne shape factor = 1, lens transmission at the respective particle size, negligible fraction of doubly charged particles from the DMA). How uncertain is the resulting CE (i.e. mass ratio)?

**A1.71** To account for these uncertainties explicitly, we have used a MonteCarlo method to estimate the absolute uncertainties of the measured AMS/CPC mass ratios, which are 29% for  $\text{NaNO}_3$  and 22% for the other 3 species. The error bars have been added to the revised Fig. 9 and corresponding explanation has been added in the caption of Fig. 9, as shown below.



**FIG. 9** Ratio of mass concentration between AMS and CPC measurements (CE) from four inorganic species (dried monodisperse particles) of (a) 300 nm  $\text{NH}_4\text{NO}_3$ ; (b) 250 nm  $(\text{NH}_4)_2\text{SO}_4$ ; (c) 300 nm  $\text{NaNO}_3$ ; (d) 300 nm  $\text{NH}_4\text{Cl}$ ; as a function of  $T_v$  in the SV and CV. Apparent mole ratios between anion vs cation (a3, c3 and d3) and cation vs anion (b3) are also shown (bottom row). The  $\text{NaNO}_3$  AMS/CPC ratios were corrected based on the measured lens transmission curve in Fig. S2 (see text) to account for the lens transmission loss. The orange traces in Fig. 9c1 and Fig. 9d1 are results from repeat CV experiments. The mole ratio of  $(\text{NH}_4)_2\text{SO}_4$  is  $\text{SO}_4$  vs  $2\text{NH}_4$ . RIE of sodium was assumed to be 1 here since no explicit RIE of Na has been reported to our knowledge, and since this species is both slow to evaporate and prone to surface ionization in the AMS. The grey area is the estimated absolute uncertainty (calculated by MonteCarlo error propagation) for measured AMS/CPC mass ratios, assuming 10% error for CPC counting, 15% error for DMA size-selection, 5% for shape factor, 10% for RIE, and 15% error for lens transmission. Lens transmission error is only applied in the error calculation of  $\text{NaNO}_3$  calculation. Finally, a total uncertainty of 29% is estimated for  $\text{NaNO}_3$  and 22% for the others.

**R1.72** L519: The provided vaporizer temperatures (300\_C for CV and 500\_C for SV) are not the temperatures where the AMS/CPC mass ratio increases (as stated in the text) but where the maximum or plateau is reached.

**A1.72:** We have changed “increased” to “peaked”

**R1.73** L522: What does the “right” in the parenthesis mean?

**A1.73:** This was a typo. “right” has been deleted.

**R1.74** L522-524: Also for this species faster decay of the signal when the particle beam is closed is observed for the CV compared to the SV. It makes no sense that this is due to faster vaporization as stated further above. Could it be that the SV scatters particles onto nearby surfaces of the ion source which are sufficiently hot to slowly vaporize the material while the CV can only emit particles in the direction from where the particles came from?

**A1.74:** The manuscript did not provide an interpretation of this trend. For a less volatile species such as NaNO<sub>3</sub>, the reviewer’s interpretation does make sense. We have revised our manuscript to include it as follows:

**“This difference may be due to the geometry of CV inhibits the particle bounce out of vaporizer to the surrounding colder ionizer surfaces, while this effect can lead to a slowly evolving signal in the SV.”**

**R1.75** L524-526: Here it is stated that the plateau of AMS/CPC mass ratio for NaNO<sub>3</sub> being less than 1 in the CV is probably due to the uncertainty of the particle lens transmission loss correction. Of course this could be the case but this is not a strong argument. The fact that the mass ratio exceeds 1 significantly for lower Tv points rather towards a correction which is too large instead of too small. In addition, there is no significant difference in the ratios for CV and SV for large Tv. So if the correction factor needs to be larger this would result in CE=1 also for the SV for this particle size. To avoid this uncertainty, it would be desirable to perform these measurements with smaller particles and not to apply a correction for lens transmission.

**A1.75:** We understand the reviewer’s concern. The detailed reason for using 300 nm NaNO<sub>3</sub> for this CE measurement has been addressed in response A1.61. Based on the data we obtained, we

have estimated the absolute uncertainty of AMS/CPC mass ratios based on MonteCarlo error propagation, which has been shown in response A1.71. The uncertainty estimates do support the statement that the plateau in the AMS/CPC mass ratio is not different from 1 within the estimated uncertainties.

**R1.76** L533: Na has a melting point of 98\_C and a boiling point (at ambient pressure) of 890\_C. I would not call this a “refractory species”. In addition, NaO should probably be Na<sub>2</sub>O.

**A1.76:** We have changed “**refractory**” to be “**semi-refractory**”, and “**NaO**” to be “**Na<sub>2</sub>O**”.

**R1.77** L545: Does the word “reproducibly” mean that these measurements were performed multiple times or does it mean that there is no Tv-dependence in this temperature range? I would disagree with the latter, there is a clear maximum visible around Tv=500\_C. In addition: “Fig. 11” should be “Fig. 9”.

**A1.77:** It means we did the measurements multiple times. We have clarified this sentence to read:

**“In the CV, AMS/CPC mass ratios of SO<sub>4</sub> were reproducibly 0.7-0.8 at T<sub>v</sub> = 400-700°C (based on multiple experiments).”**

**R1.78** L549: Replace “: : : inside CV cavity : : :” with “: : : inside the CV cavity : : :”.

**A1.78:** Revised

**R1.79** L550: Collection efficiency is compared for the CV (0.7-0.8) and the SV (0.2-0.55). This is an unfair comparison since different Tv-ranges were used for comparison. If the same ranges were used it would be either CV: 0.05 – 0.8, SV: 0.2 – 0.55 or CV: 0.7 –0.8, SV: 0.45 – 0.55.

**A1.79:** We have changed the CE range of SV to be “**0.45-0.55**”

**R1.80** L550-554: Again the faster decay of the signal (here for SO<sub>4</sub>) only makes sense if the origin of the signal is from cooler surfaces like from the ionizer surface.

**A1.80:** The detailed response to this item is the same as for response A1.74. We have added one sentence to explain this in the main text:

**“As discussed above, the faster decay of signals in the CV is likely due to the lower fraction of particles bouncing to the surrounding ionizer cage than with the SV.”**

**R1.81** L555: The decrease of AMS/CPC mass ratio is not observed for  $T_v > 700$ \_C only but starts already around 550 C.

**A1.81:** We have changed the “**decrease**” to be “**lower**” to reflect the fact that AMS/CPC ratio is lower than those at medium  $T_v$  (500-600 °C).

**R1.82** L557: Remove “the” in “due to the particle bounce”.

**A1.82:** Removed

**R1.83** L563-574: If the high background signal and the long response times for the SV are due to slow vaporization it makes no sense that for the same  $T_v$  both is improved in the CV, even though the temperature is the same (no faster vaporization) and the geometry would probably cause an opposite effect.

**A1.83:** See details in responses A1.74 and A1.80. We have clarified this sentence to be:

**“AMS/CPC mass ratios of Cl from  $\text{NH}_4\text{Cl}$  (300 nm) in the SV were reproducibly 0.2-0.25, possibly due to particle bounce onto and slow evaporation of bounced particle from the ionizer cage surfaces.”**

**R1.84** L579-584: The low  $\text{NH}_4$  background and short decay lifetimes contradict the assumption of slow vaporization of some of the substances. It is unclear to me how the anions could vaporize slower than the cations. There must be another effect affecting the anions (e.g. interaction with the surface of the vaporizer) to explain this behavior.

**A1.84:** It has been observed before that  $\text{NH}_4$  evaporates faster than the anion when aerosols are heated. One independent piece of evidence is that during SOAR and MILAGRO field studies, the  $\text{NH}_4$  balance (measured  $\text{NH}_4$ /predicted  $\text{NH}_4$ ) decreased from ~ 0.9 to 0.2 with thermodenuder temperature increases (50-260 °C), indicating an earlier evaporation of  $\text{NH}_4$  than the corresponding anions ( $\text{NO}_3$  and  $\text{SO}_4$ ) (Huffman et al., 2009). We have revised our sentence to point out this piece of evidence:

**“In the beam open/blocked experiment, the decay lifetime of NH<sub>4</sub> was below 1-2 s, which was similar or faster than the anion decays. The faster vaporization of NH<sub>4</sub> than for the anions has also been reported before for evaporation of ambient aerosols in a thermodenuder, where aerosols became more acidic when heated (Huffman et al., 2009).”**

**R1.85** L586: Replace “: : : decay lifetime (<2s) at medium T<sub>v</sub> : : :” with “: : : decay lifetime (<2s) as at medium T<sub>v</sub> : : :”.

**A1.85:** Revised

**R1.86** L587-588: The decay lifetimes of the various substances cannot be explained by their vaporization time constants (then the NH<sub>4</sub>NO<sub>3</sub> should have shorter lifetimes than the others) or by particle bounce (then the sulfate which bounces deeper into the cavity of the vaporizer should have longer lifetimes than the nitrate-related NH<sub>4</sub>). There must be another effect causing this behavior.

**A1.86:** We agree with reviewer’s comment. However, we cannot think of an explanation that satisfies *all* the available pieces of evidence. Thus we revised our sentence to explain this:

**“NH<sub>4</sub> decay in the CV at low T<sub>v</sub> (~200-330°C) exhibited a  $\tau$  ~16s for NH<sub>4</sub>NO<sub>3</sub>, ~2s for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 10s for NH<sub>4</sub>Cl, which was longer than NH<sub>4</sub> in the SV under similar low T<sub>v</sub> range. The longer NH<sub>4</sub> decay suggested slower release of NH<sub>3</sub>(g) for the CV than the SV at this low T<sub>v</sub> range (< 350°C), the reasons for which are unclear.”**

**R1.87** L596-607: Wouldn’t one also expect a variation of the NH<sub>3</sub> fragmentation pattern as a consequence of more thermal decomposition in the CV, similar to what is found for the anions? If actually intact salt molecules would be vaporized (as suggested by Murphy, 2016), why would one expect a variation in fragmentation patterns? In all cases fragmentation would probably occur then in the electron cloud which does not differ for different salts. However, another argument against the suggestion by Murphy, 2016 could be added: As shown in Figure 9 there is a completely different behavior observed for the anions and NH<sub>4</sub> (e.g. Figure 9a3, c3, d3) when T<sub>v</sub> or the vaporizer type changes. This shows quite clearly that the separation of NH<sub>4</sub> and the anions already occurs on the vaporizer and not in the ionization process.

**A1.87:** We have consolidated the text from P15 L340-349 and P26 L595-607 into a single location (in section 3.2), to make it easier to clarify this text. We have then reworded the combined text as follows to address this comment:

### **Implications for vaporization mechanisms in the AMS**

It has recently been suggested that a major fraction of  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  vaporize as intact salts in the AMS (Murphy, 2016a, 2017). Separate vaporization to  $\text{NH}_3(\text{g})$  and  $\text{H}_x\text{NO}_y(\text{g})$  followed by their separate ionization can explain the high similarity of the ammonium fragmentation pattern to that of  $\text{NH}_3(\text{g})$  in the NIST EI database (Linstrom and Mallard, 2016) (Fig. 4). It can also explain constancy of the fragmentation pattern of ammonium across vaporizers and  $T_v$  (Fig. 4), despite major simultaneous changes on the observed fragmentation patterns of sulfate and nitrate. This very different fragmentation behavior and trends between cation and anion would be unexpected if inorganic species vaporized as intact salts. If molecular salts were vaporized, species such as  $\text{NH}_4\text{NO}_3^+$ ,  $(\text{NH}_4)_2\text{SO}_4^+$ , and  $\text{NH}_4\text{Cl}^+$  would form after ionization. Since the fragmentation chemistry of molecular cations is highly dependent on the species (e.g. McLafferty and Turecek, 1993), each would fragment in characteristic ways, leading to consistent trends for the cation and anion, and potentially leading to some differences in the product ions from ammonium. The different  $\tau$  of  $\text{NH}_4$  and its associated anions after blocking the particle beam (Figs. 10-11) also suggests that thermal decomposition, followed by separate interactions with hot surfaces, is an important step in particle detection in the AMS. Section S1 in the Supp. Info. further summarizes the evidence on this topic.

**R1.88** L609: The “\_” is written as subscript.

**A1.88:** Revised

**R1.89** L621: How are the rise times defined?

**A1.89:** The rise time was defined as the time interval between 10% peak height (for avoiding interferences from the noise background) to the peak point. We have added this definition to the manuscript:

**“The rise time is defined as the time interval from 10% of peak height until the peak.”**

**R1.90** L624-625: The authors state that although lower sizing resolution are obtained with the CV, size distributions can still be measured with this vaporizer. The authors should discuss how the slower escape of the vapor from the CV affects the measured particle diameters (not only the width of the distribution).

**A1.90:** We have added the following sentences to the manuscript:

**“The lag of the particle detection times indicates that a CV-specific particle size calibration is needed, as substantial errors would arise if using a calibration curve from the SV. The lag time between CV and SV are different for different species (e.g., 0.5 ms for NO<sub>3</sub> and 1.3 ms for SO<sub>4</sub>), which suggests the CV could benefit from different size calibration curves for externally mixed aerosols.”**

**R1.91** L641-642: The references to the panels on Figure 13 are wrong.

**A1.91:** Sorry for this mistake. The references have been revised.

**R1.92** L646: The transition temperature is not the “ $T_v$  above which particles show a narrow distribution” but the  $T_v$  above which the measured particle distribution is not broadened by vaporization effects.

**A1.92:** Thanks for this suggestion. We have revised the sentence to read:

**“Transition  $T_v$  ( $T_{v,t}$ ) is defined as the  $T_v$  above which the measured particle distribution is no longer broadened by slow vaporization effects.”**

**R1.93** L650-651: Replace “: : : similar to the reported melting point trends : : :” with “: : : similar to the order of reported melting points : : :”.

**A1.93:** Revised

**R1.94** L655-657: The explanation given for the lower transition temperature for NaNO<sub>3</sub> in the CV, compared to the SV (due to longer residence time and more collisions between particle and

vaporizer surface in the CV compared to SV) does not make sense: At a temperature below the transition temperature particles on the SV can either vaporize slower or bounce. Particles that vaporize slower would also vaporize slower on the surface of the CV which is at the same temperature. This should not cause any difference in the width of the size distributions. If at all, the size distribution measured with the CV should be broader due to the geometry of the CV. Particles that bounce off the vaporizer do not contribute to the measured size distribution and thus cannot broaden the size distribution. Therefore also here a possible explanation of the behavior is bounce of particles off the SV onto nearby relatively warm ionizer surfaces from where they desorb more slowly. This could also explain the broadening of the size distributions for very large  $T_v$  (L667-669).

**A1.94:** We note that the reviewer's statement that "particles that bounce off the vaporizer do not contribute to the measured size distribution and thus cannot broaden the size distribution" is incorrect. Robinson et al. (2017) have recently shown that particles that bounce (delayed particles) do contribute to the size distribution signal, and especially to the tail of the size distribution, However the next statement from the reviewer appears to contradict that statement and be consistent with the findings of Robinson et al. (2017). We have revised our sentence as:

**"The lower  $T_{v,t}$  of NaNO<sub>3</sub> was probably due to less particle bounce and thus less delayed particle signals (Robinson et al., 2017) in the CV than SV."**

For the higher  $T_v$ , we did not observe this broadening effect in the SV but only CV. The explanation of slow desorption from the nearby ionizer surfaces cannot explain why this broadening is only found in the CV and not SV. We have removed our original tentative explanation of "**increased surface interactions**" from the paper.

**R1.95** L660: I would be careful calling it a "linear relationship" what is presented in Figure 14: For  $T_m$  there is rather a square relationship;  $T_b$  is the temperature at which the vapor pressure reaches ambient pressure. This is not needed for boiling under the conditions found on the vaporizer.

**A1.95:** We have removed the "linear" in the manuscript. It is true that the vaporization temperature is lower than its boiling temperature. While vaporization temperature and boiling temperature are

positively correlated, we just use the  $T_b$  as an indication of vaporization temperature for different species here.

**R1.96** L671: Replace “decomposition rates” with “vaporization and decomposition rates”.

**A1.96:** Revised.

**R1.97** L675: In the SV the peak widths are all even within 0.5 ms.

**A1.97:** Changed to be “**0.5 ms**”.

**R1.98** L682: “Figure 13c1-2” should be “Figure 13b1-2”.

**R1.98:** Changed.

**R1.99** L682-683: There is no data on ambient size distribution measurements and therefore I do not think it is adequate to draw conclusions about the applicability of the CV for such measurements. In addition, no discussion is provided on how the CV has an impact on the sizing of the aerosol, by delayed measurement of the particles.

**A1.99:** We submitted a second paper (after this one) to Aerosol Science and Technology (AS&T) on comparing the performance of SV and CV in field studies. This paper went through a faster review and revision process, and is published now.

Hu, W., Campuzano-Jost, P., Day, D. A., Croteau, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L. (2017). Evaluation of the new capture vaporizer for aerosol mass spectrometers (AMS) through field studies of inorganic species, *Aerosol Sci Tech*, 0-0, 10.1080/02786826.2017.1296104

In that paper, the ambient size distribution is investigated. Thus we cite that paper for this point:

**“However, size distributions in ambient air tend to be broad, and with the size calibration curve of  $(\text{NH}_4)_2\text{SO}_4$  applied, consistent size distribution measurement between the SV and CV is found, suggesting the size distribution measurement in the CV is still useful (Hu et al., 2017b).”**

**R1.100** L686-687: I wonder how the PToF/MS mode signal ratio can provide quantitative information on vaporization rates.

**A1.100:** We have changed “quantify” to “study”.

**R1.101** L693: “Fig. 13c3” should be “Fig. 13a3”.

**A1.101:** Changed

**R1.102** L696: “Figs. 13c1-c3” should be “Figs. 13b1-b3”.

**A1.102:** Changed.

**R1.103** L702: “reduced” is not adequate here. Fragmentation at 500-550 °C is not reduced (compared to SV measurements) but only less increased (compared to higher Tv).

**A1.103:** Revised.

**R1.104** L725: The bounce fraction is not reduced in the CV (the particles still bounce, but they bounce into the cavity), only the fraction of particles lost due to bounce is reduced.

**A1.104:** We have revised this sentence to be:

**“...indicating reduced fraction of particle loss due to bouncing in the CV.”**

**R1.105** L725-729: This is speculation and should not be in the conclusions.

**A1.105:** We have now published this result by comparing SV and CV AMSs with PILS-IC and SMPS during field studies. We cite our AS&T paper (see details in the response A1.99) to support this point. We think it is important to keep this in the conclusions, as this is a critical future in terms of the future use of the two vaporizers. The revised sentence is shown below:

**“Although the CE of some pure inorganic species were still less than 1 in the CV, a higher CE(~1) has been observed for ambient internally mixed particles (Hu et al., 2017b)”**

**R1.106** L734-735: This shows that the numbers provided in this paragraph are highly dependent on the vaporizer history.

**A1.106:** We have added a note to remind readers of this important point:

**“Note that these CO<sub>2</sub><sup>+</sup>/NO<sub>3</sub> ratios can be highly dependent on each individual instrument and its recent sampling history.”**

**R1.107** L736: “: : should much smaller than for the SV, : : :” should be replaced by “: : : should be much smaller for the CV than for the SV, : : :”.

**A1.107:** Revised.

**R1.108** Conclusion: I am missing a fair and critical assessment of the CV in this final section. The conclusion sounds too positive to me and does not sufficiently include the limitations and drawbacks of the CV.

**A1.108:** We have revised our conclusion to remove the speculation, as shown in responses A1.99 and A1.105. We agree that an overall assessment of the advantages and limitations of the CV is important. We included such an assessment in the form of a Table (shown below) of our AS&T paper (Hu et al., 2017) based on the results shown in both this paper and the AS&T paper. It is an accident of the review process that the AS&T paper was published before this one.

Excellent
  Acceptable
  Less desirable

	SV	CV
CE for ambient particles	Middlebrook et al. (2012)	CE=1
CE for pure inorganics in lab	Variable bounce fraction	<=1 but better than SV
Slowly evolving signals from bounced particles on colder ionizer surfaces	Significant	Nearly eliminated
Ambient size distribution	Good resolution	Sufficient resolution
Lab & Chamber size distribution	Good resolution	Low resolution for monodisperse particles
Single particle IE calibration	Routinely doable	Not yet demonstrated
CPC-based IE calibration	Routinely doable	Routinely doable
Extent of thermal decomposition	Significant	Greater than SV
Nitrate quantif. (organic vs. inorganic)	Useful even under low S/N	Less contrast and lower S/N
SO <sub>4</sub> UMR quantification under high OA	More OA interferences	Lower OA interferences
Nitrate → CO <sub>2</sub> artifact (“Pieber effect”)	Important in some cases	Much lower for AN, similar for SN
Nitrate → Chloride artifact	Observable but small	Smaller than SV

**R1.109** Table 1: In the headline “Ions” should be “Ion” and “Parent ions” should be “Parent ion”.

**A1.109:** Changed.

**R1.110** Some of the numbers in the table have too many digits. E.g., 33.19 +/- 0.53 is rather 33.2 +/- 0.5.

**A1.110** Per reviewer’s suggestion, we have reduced the number of digits when appropriate. The revised table is shown below:

**Table 1. Fragmentation patterns of particulate nitrate from NH<sub>4</sub>NO<sub>3</sub> particles and particulate sulfate from (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles. Both fragmentation patterns were measured in pure argon gas. The intensity relative to the largest peak and the fraction of total are reported. The uncertainties of the fragment fractions correspond to the variability of the data as one standard deviation.**

UMR Mass	Mass HR Mass	Fragment Ion <sup>a</sup>	Parent ion	Rel. intensity			Fraction (%)		
				CV <sup>b</sup>	SV <sup>b</sup>	SV Lit. <sup>c</sup>	CV <sup>b</sup>	SV <sup>b</sup>	SV Lit. <sup>c</sup>
					NH <sub>4</sub> NO <sub>3</sub>				

30	29.9980	NO <sup>+</sup>	NO <sup>+</sup>	100.0	100.0	100.0	92.5±1.1	72.9±3.8	56.5±4.6
46	45.9929	NO <sub>2</sub> <sup>+</sup>	NO <sub>2</sub> <sup>+</sup>	7.5	34.8	74.9	6.9±1.1	25.3±4.3	42.2±8.0
63	62.9956	HNO <sub>3</sub> <sup>+</sup>	HNO <sub>3</sub> <sup>+</sup>	0.1	0.9	0.9	0.1±<0.1	0.1±<0.1	0.5±0.1
					(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>				
16	15.9949	O <sup>+</sup>	O <sup>+</sup>	6.1	8.6	0.7	2.0±0.2	2.1±0.6	0.2±<0.1
17	17.0027	HO <sup>+</sup>	HO <sup>+</sup>	20.8	22.9	16.8	6.9±0.6	5.7±0.2	4.2±0.3
18	18.0106	H <sub>2</sub> O <sup>+</sup>	H <sub>2</sub> O <sup>+</sup>	91.1	100.0	78.2	30.2±0.9	25.0±0.6	19.8±1.6
24	23.9835	SO <sub>2</sub> <sup>+</sup>	SO <sup>+</sup>	0.5	0.6	0.6	0.2±<0.1	0.1±<0.1	0.2±<0.1
32	31.9721	S <sup>+</sup>	S <sup>+</sup>	8.1	9.8	14.1	2.7±0.3	2.5±0.8	3.6±0.1
48	47.967	SO <sup>+</sup>	SO <sup>+</sup>	60.1	78.1	67.1	19.9±0.4	19.5±0.3	17.0±0.4
49	48.9748	HSO <sup>+</sup>	HSO <sup>+</sup>	<0.1	0.4	N/A	<0.1	0.1±<0.1	N/A
50	49.9826	H <sub>2</sub> SO <sup>+</sup>	H <sub>2</sub> SO <sup>+</sup>	<0.1	0.2	N/A	<0.1	0.1±<0.1	N/A
64	63.9619	SO <sub>2</sub> <sup>+</sup>	SO <sub>2</sub> <sup>+</sup>	100.0	85.8	100.0	33.2±0.5	21.4±0.4	25.3±1.5
65	64.9613	j <sup>33</sup> SO <sub>2</sub> <sup>+</sup>	SO <sub>2</sub> <sup>+</sup>	0.9	0.7		0.3±<0.1	0.2±<0.1	
65	64.9697	HSO <sub>2</sub> <sup>+</sup>	HSO <sub>2</sub> <sup>+</sup>	0.2	6.1	5.7	0.1±<0.1	1.5±0.1	1.4±0.2
80	79.9568	SO <sub>3</sub> <sup>+</sup>	SO <sub>3</sub> <sup>+</sup>	<0.1	38.0	56.7	0.9±<0.1	9.5±0.1	14.3±2.2
81	80.9562	j <sup>33</sup> SO <sub>3</sub> <sup>+</sup>	SO <sub>3</sub> <sup>+</sup>	2.7	0.3		0.1±<0.1	0.1±<0.1	
81	80.9646	HSO <sub>3</sub> <sup>+</sup>	HSO <sub>3</sub> <sup>+</sup>	0.2	23.8	26.2	0.4±<0.1	5.9±0.1	6.6±0.5
82	81.9725	H <sub>2</sub> SO <sub>3</sub> <sup>+</sup>	H <sub>2</sub> SO <sub>3</sub> <sup>+</sup>	<0.1	0.3	N/A	<0.1	0.1±<0.1	N/A
96	95.9517	SO <sub>4</sub> <sup>+</sup>	SO <sub>4</sub> <sup>+</sup>	<0.1	<0.1	N/A	<0.1	<0.1	N/A
97	96.9418	HS <sub>2</sub> O <sub>2</sub> <sup>+</sup>	HS <sub>2</sub> O <sub>2</sub> <sup>+</sup>	<0.1	<0.1	N/A	<0.1	<0.1	N/A
97	96.9596	HSO <sub>4</sub> <sup>+</sup>	HSO <sub>4</sub> <sup>+</sup>	<0.1	0.1	N/A	<0.1	<0.1	N/A
98	97.9674	H <sub>2</sub> SO <sub>4</sub> <sup>+</sup>	H <sub>2</sub> SO <sub>4</sub> <sup>+</sup>	0.1	12.6	16.7	0.3±<0.1	3.1±0.1	4.2±0.5

<sup>a</sup> All the isotope ions are calculated based on isotope ratios in fragmentation table, thus not shown here, which account for ~1% of nitrate and ~3% of sulfate in the SV and ~0.5% of nitrate and ~3% in sulfate in the CV. <sup>b</sup> This study; <sup>c</sup> from Hogrefe et al. (2004).

**R1.111** Table 2: I suggest replacing “Fragmentation table : : :” with “Changes of the fragmentation table ...”.

**A1.111:** Revised.

**R1.112** Figure 1: “SMPS” should be “DMA”. It would be helpful if some dimensions would be added in panel a).

**A1.112:** Figure 1 has been revised. Corresponding dimensions have been added, please see updated Fig. 1 in response A1.11.

**R1.113** Figure 2-15: Units should be provided after a “/”, not in parentheses.

**A1.113:** Based on a quick survey, it seems that papers published in the AMT generally use parentheses rather than “/” to label units. For example see two recently published AMT papers:

<http://www.atmos-meas-tech.net/10/351/2017/>; <http://www.atmos-meas-tech.net/10/333/2017/>.

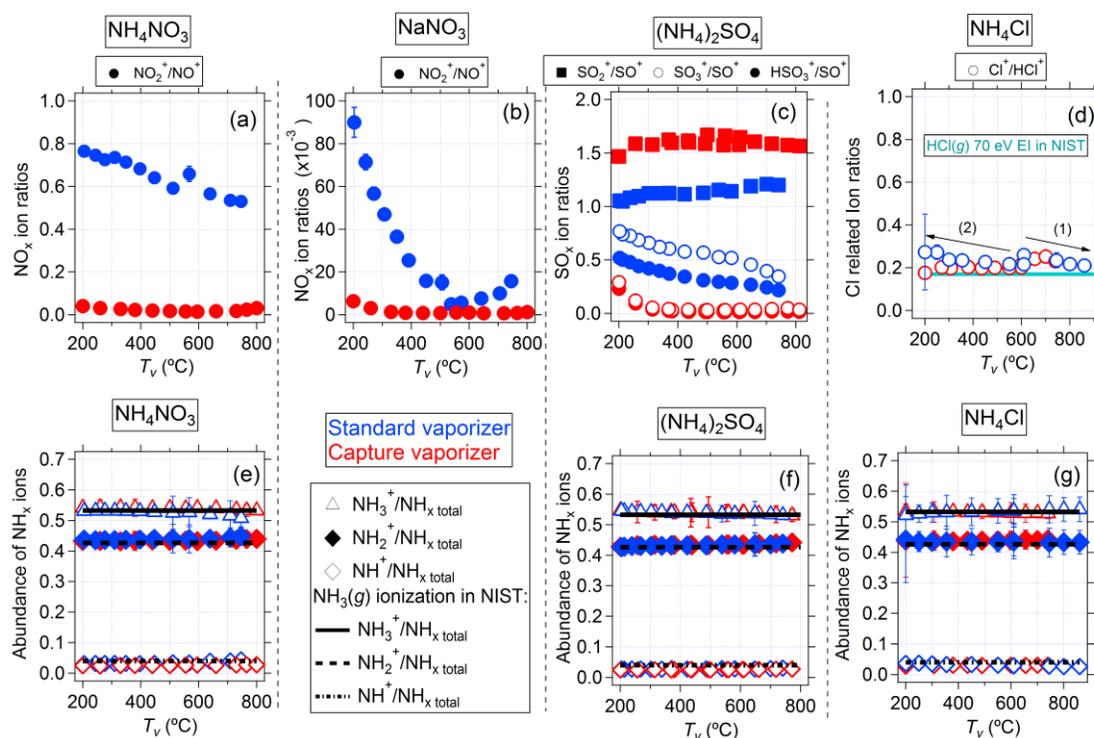
Thus, we have kept the original unit labeling here.

**R1.114** Figure 2: Add “(FWHM)” after “Peak width” in the Figure caption. Replace “: : : which is a transition : : :” with “: : : where a transition : : : occurs : : :”.

**A1.114:** “(FWHM)” has been added to the graph. The caption of figure 2 has been revised. Please see updated Fig.2 in the response A1.20.

**R1.115** Figure 4: Shown are ion ratios not “fragmentation patterns” as stated in the caption. Error bars are standard deviations of what? The different line types used for the  $\text{NH}_x/\text{NH}_{x,\text{total}}$  ratios cannot be seen in the graphs; in the legend there is twice “ $\text{NH}_2^+/\text{NH}_{x,\text{total}}$ ”.

**A1.115:** The caption and graph have been changed according to the reviewer’s suggestions.



**Fig. 2** Ion ratios of pure inorganic standard species vs  $T_v$  for the SV and CV: (a) and (e)  $\text{NH}_4\text{NO}_3$ , (b)  $\text{NaNO}_3$ , (c) and (f)  $(\text{NH}_4)_2\text{SO}_4$ , and (d) and (g)  $\text{NH}_4\text{Cl}$ . Error bars are standard deviations. For the  $\text{NH}_4\text{Cl}$  experiment, we first increased  $T_v$  from  $600^\circ\text{C}$  (arrow labeled 1) in both the SV and CV, then tuned back to the  $600^\circ\text{C}$ , and decreased the  $T_v$  to  $200^\circ\text{C}$  (arrow 2).

**R1.116** Figure 5 and 6: Not only  $\text{NO}_2^+/\text{NO}^+$  is shown in the graphs (as stated in the caption) but also  $\text{NH}_2/\text{NH}$  and  $\text{NH}_3/\text{NH}$ . Replace “hit” with “hits” in L806/814 and “particle” with “particles” in L807/815. In L806/813 “a” should be added between “are” and “rough”. Why are data points missing in Figure 6 for  $\text{NH}_x/\text{NH}$  on both ends of the graph?

**A1.116:** Captions of Fig. 5 and Fig. 6 have been revised based on the reviewer’s suggestions. Since the captions of two figures are very similar, only the caption from Fig. 5 is shown below:

**“FIG. 5 CV: Particle beam position dependence of  $\text{NO}_2^+/\text{NO}^+$ , total detected nitrate,  $\text{NO}_2^+$  and  $\text{NO}^+$  signals, RIE of  $\text{NH}_4$  ( $\text{RIE}_{\text{NH}_4}$ ),  $\text{NH}_2^+/\text{NH}^+$ ,  $\text{NH}_3^+/\text{NH}^+$  and nitrate equivalent mass ratio of  $\text{CO}_2^+/\text{NO}_3$ . The shaded areas are a rough indication for where the particle beam hits the vaporizer. A constant IE obtained with pure  $\text{NH}_4\text{NO}_3$  particles at the center of the lens was applied to all data collected in this experiment. The particle size-resolved detection for the edge and center positions are shown in Fig. 7.”**

The missing point on the edge of Figure 6 is due to the low signal-to-noise in that data, which is caused by the low signal-to-noise level for the Q-AMS we used in this experiment. See response A1.44 for further details on that point.

**R1.117** Figure 7: The position data referenced in the caption do not mean much if no reference is given. What does “double charged 300 nm particles selected by DMA” mean?

**A1.117:** We have added the dimension values to the Figure 1 (see updated Fig.1 in the response 1.11), which will give a rough idea on where those positions are. The confusing sentence has been revised, as the sentence underscored shown:

**“Size-resolved detection of  $\text{NH}_4\text{NO}_3$  (DMA selected 300 nm particles, including some larger doubly charged particles) major ions using the PToF acquisition mode at (a) CV edge (position = 7.6 mm in Fig. 5), (b) CV center (position = 7.1 mm in Fig. 5), (c) SV edge (position = 8.4 mm in Fig. 6) and SV center (position = 7.9 mm in Fig. 6).”**

**R1.118** Figure 8: Replace “: : : period as shown Fig. 4a : : :” with “: : : period as those shown in Fig. 4a : : :”.

**A1.118:** Revised.

**R1.119** Figure 9: What does “: : : from four dry monodisperse particles : : :” mean? Have only four particles been measured? “were corrected with the lens transmission curve” is laboratory slang.

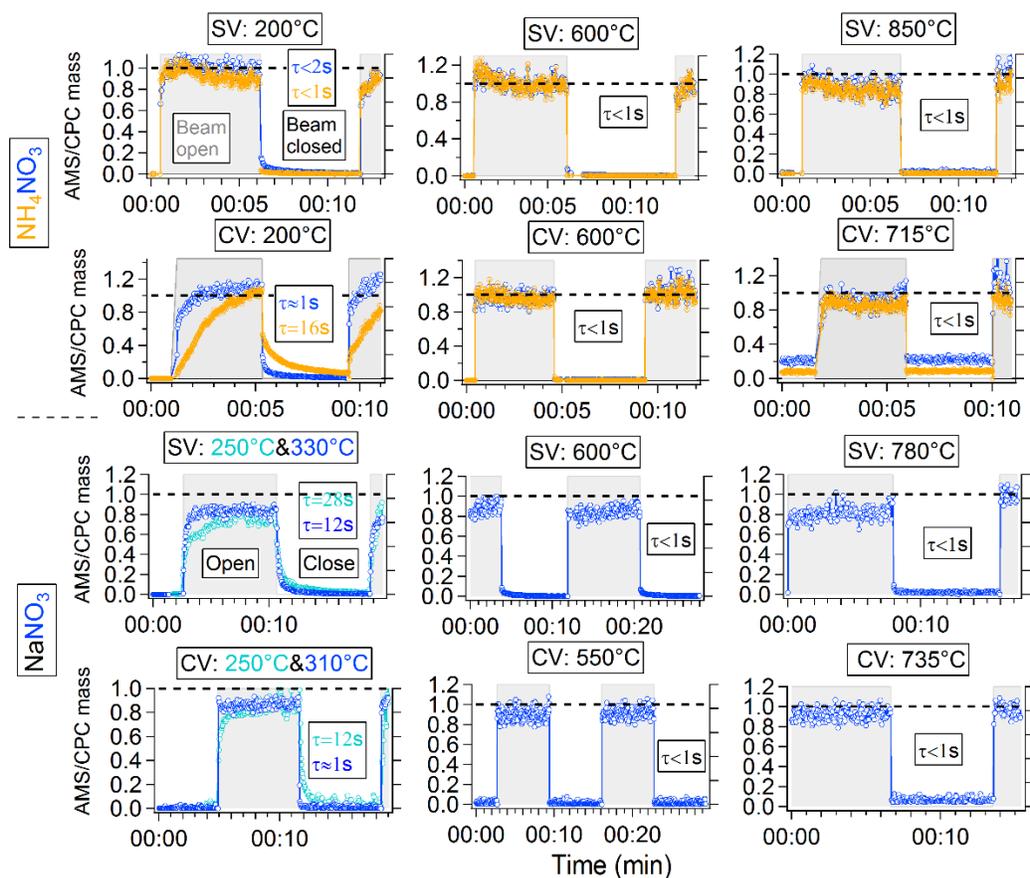
**A1.119:** The two sentences in the caption has been revised to be:

“Ratio of mass concentration between AMS and CPC measurements (CE) from four inorganic species (dried monodisperse particles) of (a) 300nm NH<sub>4</sub>NO<sub>3</sub>; (b) 250 nm (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; (c) 300 nm NaNO<sub>3</sub>; (d) 300 nm NH<sub>4</sub>Cl; as a function of T<sub>v</sub> in the SV and CV.”

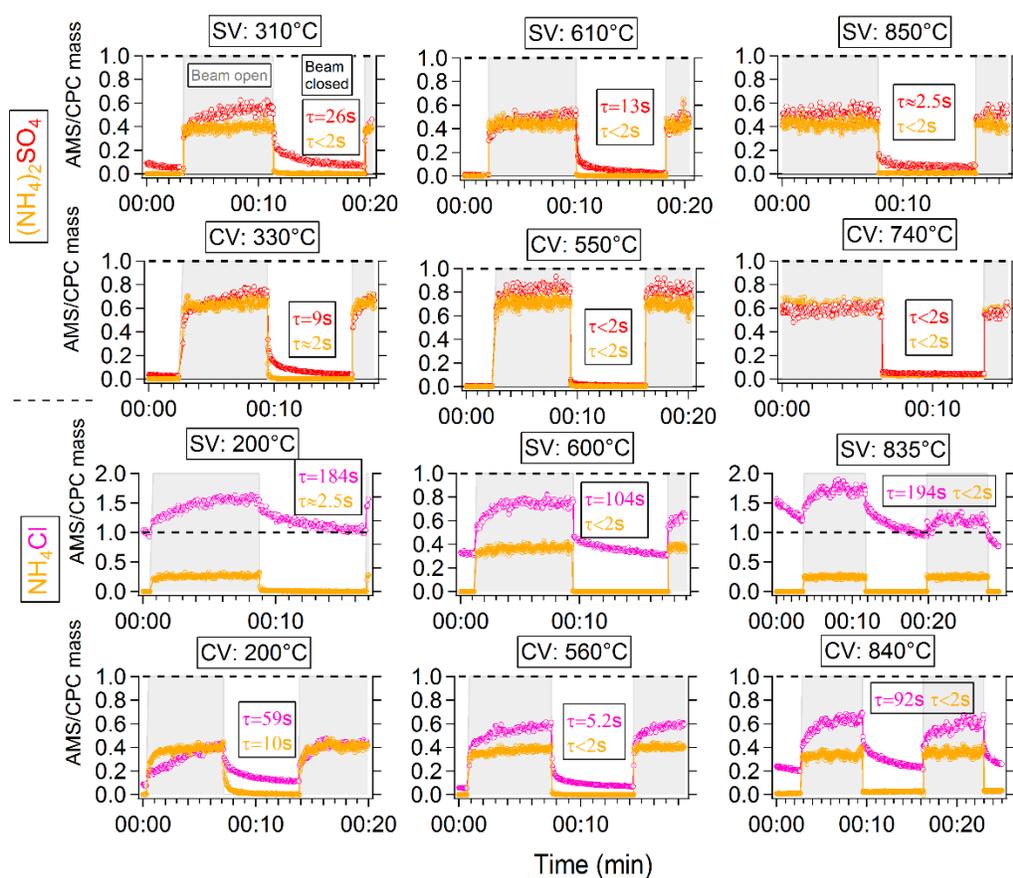
“The NaNO<sub>3</sub> AMS/CPC ratios were corrected based on the measured lens transmission curve in Fig. S2 (see text) to account for the lens transmission loss.”

**R1.120** Figure 10 and 11: Add units to the time axes. Is it seconds or minutes? In L860 replace “T” with “tau”.

**A1.120:** Unit (minutes) to the time axes has been added. “T” in Fig. 11 has been changed to be “τ”



**FIG. 10** Results of an experiment slowly alternating beam-open and beam-closed positions while sampling  $\text{NH}_4\text{NO}_3$  and  $\text{NaNO}_3$  in the SV and CV. Note that the total signal (and not just the difference signal) is shown in all panels. The results from three/four different vaporizer temperatures (low, medium and high within the usable range) for each species are shown.  $\tau$  is the lifetime of signal decay and was estimated through an exponential fit to the relevant part of the time series.  $\tau$  for the rising signal is not shown, since it always varies in the same way.



**FIG. 11** Results of an experiment slowly alternating beam-open and beam-closed positions while sampling  $\text{NaNO}_3$  and  $\text{NH}_4\text{Cl}$  in the SV and CV. Note that the total signal (and not just the difference signal) is shown in all panels. The results from three/four different vaporizer temperatures (low, medium and high within the usable range) for each species are shown.  $\tau$  is the lifetime of signal decay and was estimated through an exponential fit to the relevant part of the time series.  $\tau$  for the rising signal is not shown, since it varies in the same way.



## **Anonymous Referee #2**

**R2.0** This paper compares the efficiency of two vaporizer systems for Aerodyne AMS/ACSM.

The first one, called standard vaporizer (SV), is the vaporizer which is currently equipping all Aerodyne AMS/ACSM. The second one is a newly design vaporizer named “capture” vaporizer or CV. The capture vaporizer was designed in order to reduce/eliminate uncertainties related to particle bounce during the vaporization step. The authors focused their work on five inorganic species (ammonium nitrate, ammonium sulfate, ammonium chloride, and sodium nitrate) representative for inorganic species that can be found in ambient non-refractory particles. For each salt, influence of the vaporizer temperature on the fragmentation patterns, individual collection efficiency and particle sizing on both vaporizers were investigated. This provides a clear explanation of the processes taking place during the vaporization and ionization steps of the AMS/ACSM and the influence of the vaporizer’ type. The text is well supported by a large number of figures. This work is appropriate for AMT. However, the authors may consider the following comments before publication.

**A2.0:** We thank the reviewer for his/her review and useful comments. All of the items mentioned in this first paragraph are addressed in response to the more specific comments below, in particular R2.1-R2.3, R2.13.

Specific comments:

**R2.1 (a)** As mentioned in the introduction of the manuscript, Xu et al. (2016) already described the capture vaporizer (even if this early paper was focused on PM<sub>2.5</sub> lens). This article also included a comparison with the SV based on similar inorganic species as in the present work (NaNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) as well as investigated influences of vaporizer temperature, changes on fragmentation pattern including recommended modifications of the fragmentation table and particle sizing (PTOF-mode). In some aspects, the manuscript presents similar results as Xu et al. (2016). Therefore, the authors have to strongly emphasize their motivations, and to clearly justify what is new compared to this earlier work. A more systematic discussion should be made. For example, recommended modifications of the fragmentation table (as presented on Table 2) appears to be different from the ones presented in Xu et al. (2016), which is not discussed at all.

**A2.1:** We separate this question to be two subquestions:

(a) This paper and Xu et al. (2017) were worked on and written in parallel over a period of two years. We were generally aware of each other's work, but for such an important topic that may lead to changes in a large number of instruments that then affect hundreds of future datasets and field studies, both groups believed strongly that it was important that two research groups performed independent experiments on two sets of instrumentation, even if some of the results would overlap. Results of overlapping experiments serve to verify repeatability of CV performance. When we submitted this paper, the Xu et al. (2017) had not been published in AS&T. We cited Xu et al. (2017) paper when we first mentioned the CV in the manuscript. We did not cite that paper more extensively since reviewers typically complain about citing unpublished papers.

However, with Xu et al. (2017) focusing on the PM<sub>2.5</sub> lens and a briefer description of capture vaporizer utility, our results show a more detailed and comprehensive characterization of the CV vs SV. Importantly, our paper uses a high-resolution AMS that provides more detailed chemical information, while Xu et al. used a unit-resolution Q-AMS. For another example, Xu et al. (2017) only reported fragmentation comparison and size distribution of two standard species of NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at standard 600 °C. Temperature dependent fragmentation and size distribution of CV, targeting 4 inorganic species, is first reported in our paper. Xu et al. (2017) only show the NO<sub>2</sub><sup>+</sup>/NO<sup>+</sup> ratio for the lens alignment experiment, however, while we present a more systematic and detailed exploration including data for total signal, RIE and fragmentation of NH<sub>4</sub>, CO<sub>2</sub><sup>+</sup>/NO<sub>3</sub> ratios, and size distributions in the SV and CV. Our paper firstly reports the CE and fragmentation of NH<sub>4</sub>Cl in the CV. Per the reviewer's suggestions, we have revised our manuscript to add corresponding comparisons with Xu et al. (2017) when relevant:

**“The much lower NO<sub>2</sub><sup>+</sup>/NO<sup>+</sup> ratios in the CV than the SV are consistent with results of Xu et al. (2017).”**

**“The higher NO<sub>2</sub><sup>+</sup>/NO<sup>+</sup> ratios on the edges of CV are consistent with the results of Xu et al. (2017)”**

**“The AMS/CPC mass ratios of dry  $(\text{NH}_4)_2\text{SO}_4$  in the CV being lower than 1 is consistent with the results of Xu et al. (2017)”**

**“Compared to the SV, most PToF distributions in the CV exhibited a slower rise, and larger differences for different ions/species, consistent with results for  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  in CV from Xu et al. (2017)”**

For the fragmentation table for sulfate, we showed the values based on our experimental results. We do not know the reason why Xu et al. (2017) observed a larger coefficient of  $(\text{frag\_SO}_3[64]+\text{frag\_SO}_3[32])/H_2O^+$  and  $(\text{frag\_SO}_3[64]+\text{frag\_SO}_3[32])/S^+$  for the CV than ours. This is the only difference between our results and Xu et al. (2017). The difference is possibly caused by the different instrumentation and experimental conditions. Note the coefficient values of  $H_2O$  from sulfate do show a factor of 2-3 variation in the SV among different previous studies. However, those differences can be accounted for the RIE calibrations with sulfate, and thus will not influence the quantification of sulfate. In the paper, we have added text to remind the reader about this difference with Xu et al. (2017):

**“Higher coefficients for  $H_2O^+$  and  $S^+$  ion generated from  $SO_4$  were reported by Xu et al. (2017). The reason for the difference may be due to typical variations between instruments that have been observed before. However, since RIE calibrations utilize the fragmentation waves, these differences will be effectively accounted for in the RIE calibrations with  $SO_4$  and thus do not affect the quantification of  $SO_4$  if such a calibration is performed. These differences also suggest that fragmentation for the CV should continue to be investigated in the future studies.”**

(b) Finally, it is unfortunate that the authors did not investigate organics or inorganic-organic mixtures for example.

(b) See response A1.0 in terms of the need to limit the topics covered in this paper to make it manageable for authors, reviewers, and readers. The fact that we had 87 figure panels in the paper and that we have responded to 146 reviewer and short comments attests that the paper is of sufficient length and detail for publication.

We have investigated inorganic species in the field (which are mostly present as internal mixtures with organic species) in the recently published Hu et al. (2017) paper. See response A1.4 for more details.

The response of organic species in the CV vs SV has been investigated and is being written up for publication. We anticipate that paper will be at least as long as the present one.

**R2.2** Section 3.1: I would suggest to reorganize this section since the authors first state that measurements were made at 500-550\_C (and not at standard 600\_C) but provide an explanation for this choice only later on (section 3.1.3). Therefore, it would be better to discuss the influence of the vaporizer temperature before the fragmentation patterns at a specific vaporizer temperature.

**A2.2:** Thanks for the reviewer's suggestion. We did consider the structure suggested by the reviewer, which would address the temperature-dependent fragmentation patterns first. However, we found that the temperature-dependent ion ratios from the SV and CV in Fig. 4 contains too much information. We would need to explain the differences of ion ratios and temperature dependent trends at the same time, which necessitate combining section 3.1.1 and 3.1.4 together. This would result in a very long and difficult to read section. For example, new section will contain ~117 lines (47 lines for 3.1.1+70 lines for 3.1.4). Thus we think the current structure is easier to follow.

For clarity about why we choose the temperature used here, we have added the following sentence to the manuscript:

**“A slight lower  $T_v$  than the standard 600 °C used in the SV was chosen here. This is because lower  $T_v$  is recommended for general CV operation, as discussed below in section 3.3.2.”**

**A2.3** Moreover, is there any reason why the authors decided to work at similar temperature?

I think it would be more representative to compare the CV at 500-550\_C with the SV at 600\_C since both temperatures represent the optimal ones of the corresponding vaporizer. In this way, a clear parallel can be drawn between classical AMS/ACSM results and upcoming CV measurements.

**A2.3:** We agree that a comparison between SV at 600°C and CV at 500-550°C would be ideal, and that was the experimental plan. . We set the SV to 600°C, however, later we noticed that the AMS electronics were delivering less power than expected, as already explained in the caption of Fig. 4. Importantly, the experiments on temperature dependent ion ratios in Fig.4 show the ion ratio differences of SV between 600°C vs 500-550°C (<10%) are far less than those between SV and CV (a factor of 10). Thus, we believe that the comparison results shown here can be used to interpret the differences of ion ratios between the SV and CV.

Minor comments:

**R2.4** Line 176: Please provide a link or server location where William et al. (2010) can be found.

**A2.4:** The link has been added. The updated citation is:

**“Williams, L.: How to set your vaporizer temperature / Variability in mass spectral signatures; [http://cires1.colorado.edu/jimenez-group/UsrMtg/UsersMtg11/WilliamsAMSUsersMtg\\_2010\\_VapT.pdf](http://cires1.colorado.edu/jimenez-group/UsrMtg/UsersMtg11/WilliamsAMSUsersMtg_2010_VapT.pdf), AMS User's Meeting, Hyytiala, Finland, 2010.”**

**R2.5** Line 188: Are the CU 2014 results really needed? Although the authors provide a clear statement to explain the nature of the bias, the correction factor of 0.6 is not justified.

**A2.5** We have changed change the color of CU 2014 trace in Fig. 2 to grey. The updated Fig. 2 can be found in response A1.20. The correction (*Corrected vaporizer power = 0.6×displayed vaporizer power+0.1*) was obtained by matching the CU 2014 curve to the others as shown in Fig. 2b. This should be a reasonable correction since it is based on the same instrument (power cable, vaporizer, thermocouple are all the same) and only the power supply (“AMS EBOX”) was changed. We have added information on how to correct the CU 2014 trace in the legend of Fig. 5

**“Therefore, a correction (*Corrected vaporizer power = 0.6×displayed vaporizer power+0.1*), which was obtained by matching the CU 2014 curve to the others from SV, was applied”**

**R2.6** Line 294 & Fig. 4b: Do the authors have an explanation for the trend of NO<sub>2</sub>/NO ratio when Tv(SV) > 550\_C?

**A2.6:** We do not know the specific reason for the higher  $\text{NO}_2^+/\text{NO}^+$  ratio for  $\text{NaNO}_3$  above  $550^\circ\text{C}$ . However, this slightly increasing trend of  $\text{NO}_2^+/\text{NO}^+$  ratio at  $T_v > 600^\circ\text{C}$  has been observed in our other studies. Since this change is small and we do not have a good hypothesis for it, we have not discussed it in the manuscript.

**R2.7** Line 380: The authors speculate about change on  $\text{IENO}_3$  on the edge of the CV compare to center position. Would it be possible to directly determine the  $\text{IENO}_3$  at this position?

**A2.7:** Theoretically, it is possible to determine the  $\text{IE}_{\text{NO}_3}$  at the edge of the CV based on injecting known number concentration of  $\text{NO}_3$  particles. However, in order to obtain high signal-to-noise on these experiments, we injected high concentration of  $\text{NH}_4\text{NO}_3$  particle without trying to minimize the fraction of doubly charged particles. Thus  $\text{IE}_{\text{NO}_3}$  cannot be obtained with this dataset.

**R2.8** Line 407: Should be Fig. 7c

**A2.8:** Revised.

**R2.9** Line 424: Can the authors precise the vaporizer temperature during these 4 days? Was the temperature of the vaporizer only adjusted before the nitrate calibration?

**A2.9:** Yes, the vaporizer temperature was only adjusted over a wide range during the calibration experiments and was kept constant during the 4 days of chamber studies. This information has been added in the manuscript:

**“Those data were obtained after 4 days of exposing both AMSs ( $T_v=500-600^\circ\text{C}$ ) to  $10-1000 \mu\text{g m}^{-3}$  of SOA generated during chamber experiments, which could enhance this interference.”**

**R2.10** Line 456: I am not fully agreeing with the sentence “this is the first time that AMS CE has been reported as a function of  $T_v$ ”. It might be true for the SV but not for CV since Fig. 10 from Xu et al. (2016) shows the AMS/CPC mass loading vs. temperature for  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\alpha$ -pinene SOA (Fig. 10).

**A2.10:** We have changed this sentence to read:

**“To our knowledge, this is the first time that AMS CE has been reported as a function of  $T_v$  for SV”**

**R2.11** Section 3.2: In Fig. 10, the authors describe the decrease of the AMS signal when closing the particle beam by estimating the lifetime of the signal decay ( $\tau$ ). However, they refer to two different units in the text: decay time and  $\tau$ . It would be easier to use only one nomenclature.

**A2.11:** We have searched through the paper, and changed the “**decay time**” and “**decay timescale**” to be “ **$\tau$** ” in all instances.

**R2.12** Fig. 10 and 11: Units of the x-axis are missing.

**A2.12** Units have been added. The updated Fig. 10 and 11 can be found in response A1.120.

**R2.13** Line 548: The authors attribute CE <1 of ammonium sulfate in the CV to possible particles bounce on the edge of the CV. Does this mean that the particle beam can be slightly larger than the center of the CV, or a possible artefact?

**A2.13:** The vaporizer dimension has been labeled in the updated Fig. 1, as shown in the response A1.11. The CV has a 2.54 mm entrance opening, which is smaller than 3.81mm of SV. Based on the beam width probe experiments reported by Huffman et al. (2005), a few percent mass loss of sulfate due to the effect of particle shape in beam width ( $E_s$ ) is possible. A 22% uncertainty of AMS/CPC mass ratios was estimated based on different measurement uncertainties from SMPS-CPC and AMS systems. Details on the uncertainty calculations can be obtained in response A1.71. Corresponding information on the possible losses of particles due to bounce at the edges of the particle beam has been added to the main text:

**“The ~25% missing signal suggests that a small fraction of pure  $(\text{NH}_4)_2\text{SO}_4$  particles might still bounce on the edge of CV (interpreted as  $E_s$ ) or that they may still bounce out of the CV without evaporating inside the CV cavity.  $E_s$  probably contributes at least a few percent to  $(\text{NH}_4)_2\text{SO}_4$  mass loss in the CV based on beam width probe experiment results reported by Huffman et al. (2005) compared with the CV inlet width (2.54 mm, as labeled in Fig. 1).”**

**R2.14** Line 608: section 3.3: Could you please also mention on the text the particle diameters used for each salt?

**A2.14:** The particle diameters have been added to the main text:

**“Results from the inorganic species 250 nm (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 300 nm NH<sub>4</sub>NO<sub>3</sub>, 300 nm NaNO<sub>3</sub>, as well as of poly-dispersed organic nitrates generated from NO<sub>3</sub> radical + monoterpene chamber studies are discussed below (Fig. 12).”**

**“PTof distributions of monodisperse particles from three standard species (250 nm (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 300 nm NH<sub>4</sub>NO<sub>3</sub> and 300 nm NaNO<sub>3</sub>) in both vaporizers as a function of  $T_v$  are shown in Figs. 13a1-c1&a2-c2”**

**R2.15** Line 632: Should be Fig. 12e and g

**A2.15:** Revised

**R2.16** Line 641: Should be Fig. 13a3-c3

**A2.16:** Revised

**R2.17** Line 682: This is quite speculative. A comparison with SMPS ambient size distribution is needed to support this statement.

**A2.17:** We have cited our AS&T paper to support this statement. For further details see response A1.99.

**R2.18** Line 696: Should be Fig. 13b1-b3

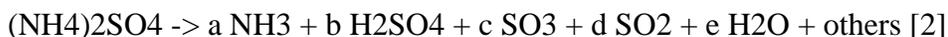
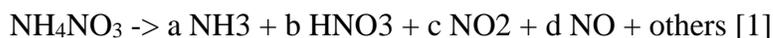
**A2.18:** Revised.

### Short comment from N. Takegawa and T. Miyakawa

**SC3.0** This manuscript presents laboratory evaluation of the standard vaporizer (SV) and newly designed capture vaporizer (CV) of an Aerodyne aerosol mass spectrometer (AMS). It is an important step toward better understanding of the physical and chemical processes in the AMS vaporizer/ionizer. We have some comments on the manuscript, which might be helpful to improve the clarity of the presentation.

**A3.0:** We thank Drs. Takegawa and Miyakawa for their useful comments. All of the items mentioned here are addressed in response to the more specific comments below.

**SC3.1 Thermal decomposition products and relative ionization efficiency (RIE).** RIE is an important parameter for the quantification, as it is the basis for estimating the ionization efficiencies of various compounds that are not directly determined by routine calibrations. RIE depends on the thermal decomposition process of aerosol particles. Figure 3 clearly indicates that major thermal decomposition products from  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  were systematically different between the SV and CV. This means that the coefficients a, b, etc. of Equation [1] and [2] were different.



The values of a, b, etc. represent the relative abundances of the thermal decomposition products in the ionization region and would be important for the interpretation of the RIE<sub>SO4</sub> values for the SV and CV (e.g., L259-262).

In order to discuss this point more quantitatively, it would be helpful to roughly estimate the values of a, b, etc. based on the fragment ratios. It may be true that the AMS ion source can produce more fragmentation than the NIST database because of the higher temperatures of neutral molecules, as the authors suggested. However, the temperature dependence of the fragment ratios in Figure 4c suggests that this effect is minor, at least for SO<sub>x</sub>. The authors could use the values of a, b, etc. from the fragment ratios, along with electron ionization cross sections, to predict the RIEs and compare them to the measured RIEs.

**A3.1:** While we agree that it would be useful to know the coefficient values of a, b c. d etc., it is not possible to unequivocally determine those coefficients from the data collected in this study. The exercise suggested might be interesting but would be very underconstrained, and in any case is far beyond the scope of this already very long paper.

In addition, while this topic is of interest from a fundamental point of view, accurate quantification can be obtained by carefully calibrating RIE, even if the molecular identity of the thermal decomposition products is not known.

### **SC3.2 Collection efficiency (CE)**

The improvement of the CE is the center of this manuscript, and we would expect more discussion on this issue. The temperature dependences of the AMS/CPC (CE) and molar ratios of acids to NH<sub>4</sub> in Figure 9 are interesting but need further investigation. The data for sulfate is not consistent with the authors' argument that the thermal decomposition of sulfate is complete in the CV at the vaporizer temperature ( $T_v$ ) of  $> 300\text{C}$  (L307-309). The authors speculate that the decreased AMS/CPC ratios for nitrate and sulfate at higher temperatures were due to interaction with the vaporizer surface (based on signals in chopper-closed mode). However, this assumption is not well supported considering the significant difference in the temperature dependence among the AMS/CPC ratios, molar ratios, and closed signals.

**A3.2:** Improving CE was the goal for the development of the CV. However, quantifying CE is an important, but not the only goal of this manuscript. Many user groups are very reluctant to adopt the CV, if its chemical detection properties are significantly worse than for the SV, even if the CV fully resolves the CE issue. Thus the characterization of the chemical detection properties represents a major fraction of what is discussed in the present paper.

We are not sure what specific findings are inconsistent according to the commenter. We do think our results are consistent with each other. With the CE of sulfate and nitrate decreasing in the CV at higher  $T_v$ , higher closed AMS/CPC mass ratios were observed in the CV, which is consistent with the elevated close signal observed in the beam open-close experiments.

### **SC3.3 Minor points**

The authors mention that the results for ammonium contradict the suggestion by Murphy (2016) (abstract, L43-44). This point is not a major conclusion of the current manuscript (but it appears so as it is written in the last sentence of the abstract). More importantly, Crehn et al. (AMT, 8, 5063-5087, 2015) showed large variability in RIE\_NH4 for various ACSMs. We suggest the sentence could be deleted.

**A3.3:** This topic has been discussed in detail in response to Dr. Murphy's short comment below.

**SC3.4** - Our recent papers regarding the development of the new particle trap and ambient intercomparison are cited in the introduction (L90-92). There are various factors affecting the ambient intercomparison result, including the collection efficiency, vaporization efficiency, choice of the calibration material, and size-cut of the aerodynamic lens. Although a regression slope of 0.7 was observed between our instrument and a sulfate particle analyzer, it was not entirely due to the CE but mostly attributed to the size-cut. Note that the definition of CE is different between our instrument and AMS because the AMS CE includes both physical collection and vaporization.

**A3.4:** We appreciate the additional information and have revised the sentence for accuracy as follows:

**“A regression slope for 0.7 of sulfate, probably caused by different size cuts in a field study, was observed between this and other instruments.”**

**SC3.5** - The manuscript presents many results, some of which are difficult to interpret or may not be very critical for demonstrating the concept of the new CV. The behavior of chloride is very complicated because of possible chemical interaction with the vaporizer (Figure 9 and 11, also Drewnick et al., AMT, 2015). The results in section 3.1.4 (beam position) and 3.1.5 (production of CO<sub>2</sub>) are interesting, but somewhat beyond the major scope of this manuscript. We suggest that these results could be removed or shortened. The quantification of chloride could be published elsewhere after the authors obtain more conclusive dataset.

**A3.5:** We respectfully disagree with the commenter's suggestion on cutting out 3.1.4 (beam position), 3.1.5 (production of CO<sub>2</sub>) and chloride quantification. Those results are important characteristics of the CV, which helps us to understand and use the CV well. They are also important for many users who will need to decide whether to adopt the CV or continue to use the

SV, as well as interpret CV datasets. The particle beam-position dependent results are helpful to understand the slower vaporization in the particle size distribution mode, by comparing the size distribution between at the edge and the centers. A lens alignment method based on those results is provided for practically using CV. The  $\text{CO}_2^+/\text{NO}_3$  is related to the oxidation state calculation in the CV. No CE of  $\text{NH}_4\text{Cl}$  in the SV and CV has been published before, to our knowledge. Our results on  $\text{NH}_4\text{Cl}$  performance in the CV and SV will be useful as a reference for the future study.

## Responses to short comment from D. Murphy

**SC4.0** The manuscript under discussion contains interesting and novel data about vaporization in the standard and capture vaporizers. The capture vaporizer shows significant promise in improving quantification in the AMS by reducing the uncertainty in collection efficiency due to particle bounce. The manuscript asserts (abstract, line 595ff) that the data support simple vaporization of ammonium to  $\text{NH}_3(\text{g})$ . These statements need to be revised. The data in the manuscript actually suggest complicated behavior for ammonium in the AMS. There are three reasons:

**A4.0:** We thank Dr. Murphy's for his comments. However, we were perplexed by many of the comments, and reached out to the commenter for clarification. In that communication we realized that the commenter had misunderstood the manuscript statements about  $\text{NH}_3(\text{g})$  detection. The manuscript made some statements based on the high similarity of the fragmentation patterns of ammonium across all temperatures and vaporizers (compared to very large simultaneous changes of the associated anions), and the high similarity to the NIST  $\text{NH}_3(\text{g})$  pattern as well. However, the commenter had understood that the statements in the paper were made based on the similarity of  $\text{RIE}_{\text{NH}_4}$  values across the two vaporizers. We do not make any conclusions based on the  $\text{RIE}_{\text{NH}_4}$  similarity, and we have clarified this in the text.

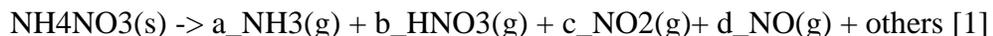
We believe that it is useful to document in the literature the responses to some of the items raised by the commenter. However, since those items are of minor importance to the central topics of this paper, we have added a new section (S1) in the Supplementary Information to capture those responses.

### **S1. Implications for vaporization and detection mechanisms in the AMS**

**It has recently been suggested that a simple model, accounting only for molecular flight through the ionizer at the vaporizer temperature, followed by electron impact ionization should completely explain SV-AMS detection (Murphy, 2016a). The high measured values of  $\text{RIE}_{\text{NH}_4}$  are difficult to reconcile with this simple model (Jimenez et al., 2016). To explain this discrepancy, it has been proposed that  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  vaporize as intact salts in the AMS (Murphy, 2016a; Murphy, 2017). The present study allows some additional considerations to be made on this topic.**

The rest of section S1 is given in response to the relevant specific comments, for ease of reading of this response document.

**SC4.1** The measured relative ionization efficiency (RIE) for ammonium in ammonium nitrate is about 4 for both vaporizers (Figures 5 and 6). According to the manuscript,



Using known electron impact cross-sections and the time spent in the ion source as a function of molecular weight, one can calculate the RIE for ammonium assuming vaporization to  $\text{NH}_3(\text{g})$  ( $a=1$ ) along with various values for  $b$ ,  $c$ , and  $d$ . There is no combination that can generate a RIE as large as 4. The simplest explanation is that the “others” term is significant. A mass-dependent sensitivity for the AMS spectrometer and detector might explain part of the high RIE but becomes very complicated because other results from the AMS would be less quantitative if there are large amounts of mass discrimination.

**A4.1:** This topic has been discussed in our recent Jimenez et al. (2016) publication. We interpret the observation of  $\text{RIE}_{\text{NH}_4} \sim 4$  (and higher) as due to processes not included in the Murphy (2016a) model, which however do play an important role in SV-AMS detection. While the hypothesis that vaporization of a major fraction of  $\text{NH}_4$  as intact salts may be appealing, we show below that it needs quite extreme quantitative assumptions to explain  $\text{RIE}_{\text{NH}_4}$ , which are unlikely to hold. This is especially true across field studies with very variable particle composition, and often with small fractions of inorganic species. It is also inconsistent with multiple observed trends in SV-AMS detection documented in Jimenez et al. (2016) and in this paper. See the responses below for further details.

Regarding mass discrimination, we have investigated this topic in response to the comment. Since to our knowledge, this topic has not been documented at all for the AMS in the peer-reviewed literature, we have added the text and figures below to the Supp. Info:

### **S1.3. Evidence against significant mass discrimination in the AMS**

**It has been suggested (Murphy, 2017) that “A mass-dependent sensitivity for the AMS spectrometer and detector might explain part of the high RIE [...],” although the same**

author stated that a large amount of mass discrimination in the AMS is unlikely (Murphy, 2016b). If the  $\text{NH}_x^+$  ions formed from ammonium were detected more efficiently than the  $\text{NO}_x^+$  (and  $\text{SO}_x^+$ ) ions, that effect could contribute to a larger-than-expected  $\text{RIE}_{\text{NH}_4}$ . Mass discrimination could arise for two reasons: (a) ions of lower  $m/z$  could be transmitted by the AMS ion optics and mass spectrometer and onto the microchannel plate (MCP) detector more efficiently; or (b) the response of the MCP detector could be substantially larger for ions of lower  $m/z$ . The first item can be evaluated by comparing the fragmentation patterns of  $\text{N}_2$  and  $\text{O}_2$  from air vs. those in the NIST mass spectral database (Fig. S6, left). Those patterns are similar on average, also consistent with measured vs. NIST  $\text{C}^+/\text{CO}_2^+$  ratios from  $\text{CO}_2(\text{g})$  (not shown). This indicates the lack of a substantially enhanced transmission favoring small  $m/z$  in the AMS. Importantly, the mass ranges involved in this comparison are the relevant ones for most of the ions formed from  $\text{NH}_4\text{NO}_3$ . For the second item, Fig. S6 (right) shows a typical result for the measured response of the MCP vs  $m/z$  as routinely acquired during the AMS threshold-setting process. We estimate that MCP response to  $\text{NH}_x^+$  ions is ~5% (10%) larger than for  $\text{NO}_x^+$  ( $\text{SO}_x^+$ ) ions, and thus it is a very small effect that can only contribute little to the high observed  $\text{RIE}_{\text{NH}_4}$ .



Figure S6. Left: comparison of the fragmentation patterns of  $\text{O}_2$  and  $\text{N}_2$  in the HR-AMS to those in the NIST database. Right: measured response of the AMS microchannel plate to single ions as a function of  $m/z$ . Only  $m/z$  at which the signal is dominated by individual ions

events, based on ion detection frequencies while analyzing the AMS background signal, are shown.

**SC4.2** The manuscript shows similar values for both vaporizers for the ratios of the sensitivity of ammonium to nitrate or sulfate, not similar values for the absolute sensitivity to ammonium. Since both nitrate and sulfate show changes, the fairly constant ratios actually imply a changing sensitivity to ammonium from one vaporizer to the other.

**A4.2:** As mentioned in response A4.0, we now understand that these comments assumed that we were making conclusions based on the similarity of  $RIE_{NH_4}$  across vaporizers. We have now clarified that this is not the case.

For completeness and to document our understanding in the public domain, we state the following (only in these responses, with no changes to the paper or Supp. Info.): A changing absolute sensitivity for all species from one vaporizer to the other is not surprising, since there are several major changes, including (a) the composition (and also likely the translational temperature) of species in the vapor plume; (b) the location and angular distribution of the vapor plume within the ionizer and relative to the electron cloud; (c) changes to the three-dimensional electric field that extracts the ions towards the mass spectrometer, due to the major impact of the vaporizer shape and voltage on that field, and due to changes in the optimal tuning of the ion source voltages; (d) changes to the three dimensional electron cloud due to the same effects in (c). In addition, a major factor for changes in sensitivity among different AMSs, or for one AMS across time periods, is the exact geometry and point of maximum emission for the electron emitting filament. Thus, even across AMSs with the same vaporizer, absolute sensitivity differences of a factor 4 are considered normal. It is expected that the *absolute* sensitivity to ammonium (and all other species) will change, given major differences in the detection system between SV- and CV- AMS, as well as due to the differences between the specific filaments used in each instrument (and other differences between the specific instruments used). Thus, the manuscript did not state that a constant absolute sensitivity for ammonium was observed when comparing SV- and CV-AMS. Also we do note that there is substantial variability in  $RIE_{NH_4}$  across different instruments (with the same vaporizer; e.g. Crenn et al., 2015) and even the same instrument in time (e.g. Salcedo et al., 2006), and trying to

extract information by comparing RIEs determined for only the two instruments used in this paper would be risky.

For ammonium nitrate, the thermal decomposition products of nitrate were clearly different between the capture and standard vaporizers (Figure 3 and lines 606-607). Different thermal decomposition products will have different masses and electron impact cross-sections and hence different sensitivities in the AMS. If the denominator (sensitivity to nitrate) in the RIE is different for the two vaporizers, then a similar RIE implies a changing sensitivity to ammonium as well.

As discussed in the previous response, we agree that the absolute sensitivity to nitrate and ammonium (and all other species), as well as the relative sensitivities, are changing between the vaporizers for many different reasons (including, but not limited to, the reasons stated by the commenter). In this paper we do not make any conclusions based on those variations, as these would have to be speculative, given that many factors are changing at the same time.

For ammonium sulfate, Figure 9c3 indicates that at 500 to 600 C the relative sensitivity of ammonium compared to sulfate was approximately the same for the two vaporizers. Lines 260-262 state that the relative ionization of sulfate compared to nitrate was up to a factor of two different for the two vaporizers. Together, these results imply a changing sensitivity to ammonium from ammonium sulfate.

It seems the commenter may be misunderstanding the figure. Figure 9a3 and 9c3 plot speciated AMS mass concentrations and mole fractions that have already been calculated from raw signal intensities after applying the relevant RIE values. This is needed in order to examine molar ratios (as opposed to signal ratios or other parameters) in those figures. Thus, the consistency of  $\text{NH}_4/\text{NO}_3$  and  $\text{NH}_4/\text{SO}_4$  between the SV and CV cannot be interpreted as suggested by this comment.

**SC4.3** The manuscript (section 3.3.1 and elsewhere) conflates evidence for thermal decomposition with the assertion that the original vaporization product of ammonium is  $\text{NH}_3(\text{g})$ . Instead, it is likely that multiple species are involved, along with thermal decomposition.

Here is a plausible explanation for the RIE of ammonium nitrate, trying to be careful to distinguish what has been measured from what is assumed:

**A4.3:** For clarity, there is no such a thing as “RIE of ammonium nitrate”. We assume the commenter is referring to the RIE of ammonium, i.e.  $RIE_{NH_4}$ , relative to nitrate (in ammonium nitrate).

a) Ammonium nitrate has been observed to vaporize in vacuum to a combination of  $NH_3(g)$ ,  $HNO_3(g)$ , and  $NH_4NO_3(g)$  [Chien et al., 2010]. We assume that those products also apply to the vaporization conditions present in the AMS.

It is incorrect to state that ammonium nitrate has been *observed* to vaporize in vacuum to  $NH_4NO_3(g)$  in any significant fraction based on Chien et al. (2010). It is also highly dubious whether the conclusions of that study, if correct, would apply to AMS conditions. The vaporization in that study was conducted at temperatures of 64-92°C, which would greatly limit thermal decomposition compared with 600°C in the AMS. In addition, a very low electron energy of only 3 eV above the ionization energy (which would greatly reduce fragmentation) was used, compared to ~60 eV (above typical ionization energies) in the AMS. Thus those detection conditions are far softer than in the AMS. Despite those very soft detection conditions, the *direct* observation of  $NH_4NO_3^+$  in that study only accounts for 0.02% of the ions detected. Thus that result can be summarized as that *under conditions far softer than in the AMS, a trace amount of actual  $NH_4NO_3(g)$  has been directly confirmed.*

Chien et al. (2010) make other statements based on an indirect method without chemical detection, but that method relies on several assumptions and simplifications of the decomposition chemistry, and thus has higher uncertainties. The result of the indirect method is that only ~22% of the  $NH_4NO_3(s)$  molecules would vaporize as  $NH_4NO_3(g)$ . Assuming that result was correct, and given that the temperature in the Chien et al. setup was much lower than in AMS, it is most likely that *at most 22% of the  $NH_4NO_3(s)$  molecules can vaporize as  $NH_4NO_3(g)$  in the AMS, although the actual fraction is likely far lower.*

b) There is thermal decomposition on the hot surfaces of the vaporizers. Thus, there will be less  $HNO_3(g)$  and  $NH_4NO_3(g)$  in the electron beam than originally vaporized. Figure 3 in the discussion manuscript shows that there is more thermal decomposition in the capture vaporizer, as expected with more wall collisions. It is worth noting that Chien et al. used a Knudsen cell with

many wall collisions and still measured significant amounts of  $\text{NH}_4\text{NO}_3(\text{g})$  effusing from the vaporizer at about 80 C, so decomposition does not occur on every wall collision.

c) We assume that  $\text{NH}_4\text{NO}_3(\text{g})$  fragments in an electron beam to produce a significant fraction of  $\text{NH}_x^+$  ions, producing a high RIE for the portion of  $\text{NH}_4\text{NO}_3(\text{g})$  that survives the vaporizer.

d) For the capture vaporizer, the data in Figure 3 suggest that much of the nitrate thermally decomposes to  $\text{NO}(\text{g})$ . If only  $\text{NO}(\text{g})$  and  $\text{NH}_3(\text{g})$  survived the wall collisions in the capture vaporizer, then the calculated RIE for ammonium would be about 2.8. An RIE of 4 can be explained as a combination of some surviving  $\text{NH}_4\text{NO}_3(\text{g})$  and some mass discrimination.

e) For the standard vaporizer, the data in Figure 3 suggest that much of the nitrate ends up as  $\text{NO}_2(\text{g})$  and  $\text{HNO}_3(\text{g})$ . The calculated RIE for  $\text{NH}_3(\text{g})$  compared to these molecules is 0.8 to 1.8. An RIE of 4 would require a factor of 2 to 5 in mass discrimination over a limited mass range, which is unlikely [Murphy, 2016b]. On the other hand, 10 to 20% of the vaporized molecules in the standard vaporizer never hit a wall. It is thus expected that in the standard vaporizer more  $\text{NH}_4\text{NO}_3(\text{g})$  will go through the electron beam and increase the RIE of ammonium. Note that with these hypotheses the fairly large RIEs for ammonium in the capture and standard vaporizers arise for different reasons. For the capture vaporizer,  $\text{NO}(\text{g})$  is a light molecule with a relatively small electron impact cross-section, so the observed large RIE is probably mostly because the denominator in the RIE is small. A small denominator would also explain the observed larger RIE for sulfate (line 606). For the standard vaporizer, the observed ammonium RIE is probably because  $\text{NH}_4\text{NO}_3(\text{g})$  (or similar molecule) is contributing to the  $\text{NH}_x^+$  signal, leading to a large numerator.

We have added the text below to the Supp. Info., showing that it does not appear possible to quantitatively explain the observed  $\text{RIE}_{\text{NH}_4}$  with this hypothesis and reasonable assumptions. Only under quite extreme assumptions, which appear unrealistic for the AMS, can a quantitative explanation work.

### **S1.1. Quantitative analysis of $\text{RIE}_{\text{NH}_4}$ when a fraction of $\text{NH}_4\text{NO}_3$ vaporizes as an intact salt**

**It has been suggested that the high  $\text{RIE}_{\text{NH}_4}$  observed in the AMS can be explained by the vaporization of intact  $\text{NH}_4\text{NO}_3$  molecules, followed by their ionization, and production of  $\text{NH}_3^+$  ions with high efficiency from that process (Murphy, 2017). However, it is very**

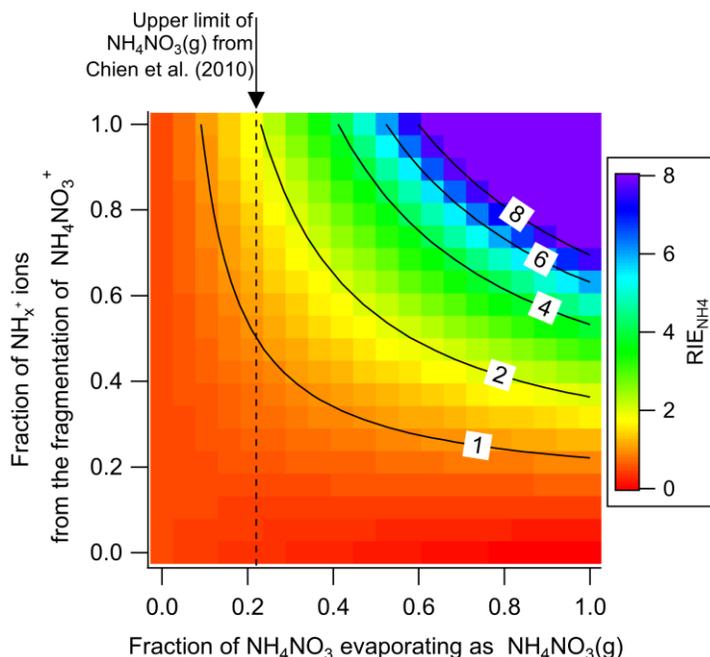
difficult to reach a typical  $RI_{NH_4}$  of 4 based on this hypothesis with reasonable assumptions. This is even more so when considering values of  $RI_{NH_4} \sim 6.2$  that are often observed in AMS instruments (Salcedo et al., 2006) or values up to 14.7 on ACSM instruments (Crenn et al., 2015). This can be shown by estimating the  $RI_{NH_4}$  that would be observed if the detection process followed the suggestion of Murphy (2017). The following numerical assumptions are used for this calculation (and some sensitivity studies are discussed below):

- a. The upper limit molar fraction of  $NH_4NO_3(g)$  estimated by Chien et al. (2010) is actually realized at the AMS vaporizer temperature of approximately  $600^\circ C$ , which is much larger than the  $64-92^\circ C$  used in those experiments:
  - a.  $NH_4NO_3 \rightarrow 78\% NH_3(g) + 78\% H_xNO_y^+(g) + 22\% NH_4NO_3(g)$
- b. The ionization efficiency of each species is approximately proportional to its molecular weight (Jimenez et al., 2003).
- c. All the species have the same average translational temperature (as implicitly assumed in Murphy et al. 2016a, 2016b), and thus that their flights times scale as  $\sqrt{MW}$ .
- d.  $1/2$  of the  $H_xNO_y(g)$  is  $NO_2(g)$  and the other  $1/2$  is  $HNO_3(g)$ .
- e. The molar fragmentation fraction for molecular  $NH_4NO_3^+$  favors  $NH_3^+$  more than proportionally to its mass fraction in the parent ion, as suggested by Murphy (2017).  
E.g.:



With those assumptions  $RI_{NH_4} \sim 1.1$ . If one assumes in (d) 100% of either  $NO_2(g)$  or  $HNO_3(g)$  for  $H_xNO_y^+(g)$ , then  $RI_{NH_4} \sim 1.05-1.12$  can be obtained. If one assumes in (e) that the fragmentation of  $NH_4NO_3^+$  yields 75%  $NH_x^+$ ,  $RI_{NH_4} = 1.5$  (if one assumes 100%  $NH_x^+$ , then  $RI_{NH_4} = 2.1$ ). Thus even with aggressive assumptions, the hypothesis is not consistent with the observed  $RI_{NH_4}$  values of 4-14. It is very likely that the  $NH_4NO_3(g)$  fraction under (a) is much lower in the AMS (due to the  $520^\circ C$  higher  $T_v$ ), probably near zero. If we assume a value of 5%, and the rest of the default assumptions above, then  $RI_{NH_4} \sim 0.7$ . Thus it seems very difficult to quantitatively explain the observed  $RI_{NH_4}$  with the Murphy (2017) hypothesis with reasonable assumptions.

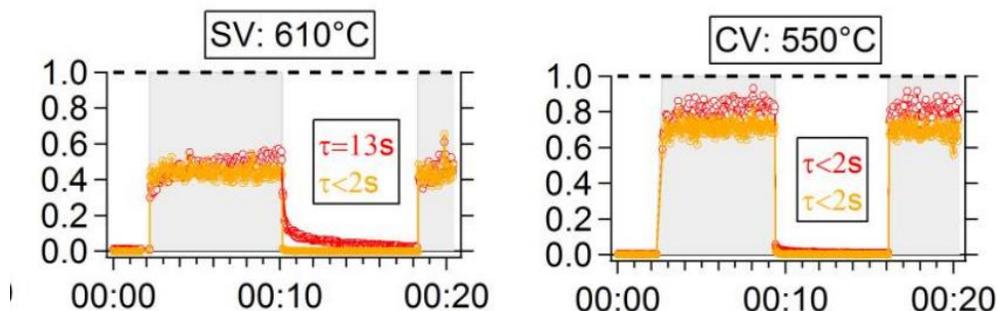
For reference, Figure S4 shows the estimated  $RIE_{NH4}$  estimated in this way as a function of the two key parameters. To obtain values of  $RIE_{NH4} = 4$  and larger, one needs to assume that a very large fraction of  $NH_4NO_3$  vaporizes as  $NH_4NO_3(g)$  (far higher than the upper limit reported at  $80^\circ C$ ), AND that the fragmentation of  $NH_4NO_3^+$  very strongly favors  $NH_x^+$  ions. Importantly, the high vaporized fraction of  $NH_4NO_3(g)$  would also need to be achieved for mixed ambient particles with high organic and low  $NH_4NO_3$  fractions, in order for this hypothesis to be consistent with ambient observations.



**Figure S4: estimated  $RIE_{NH4}$  as a function of the assumed fraction of  $NH_4NO_3$  vaporizing as  $NH_4NO_3(g)$ , and the fraction of  $NH_x^+$  ions formed from the fragmentation of  $NH_4NO_3^+$ . Also marked is the upper limit fraction of  $NH_4NO_3(g)$  evaporated at  $\sim 80^\circ C$  (Chien et al., 2010)**

Regarding the commenter's tentative explanation for  $RIE_{SO4}$ , we note that  $RIE_{SO4}$  in the CV is not always higher than for the SV, and values as low as 1.1 have been observed in CV, compared to up to 1.4 in SV (see response A1.28). We also note that the centroid of the sulfate ion signal only changes from  $m/z$  66 (SV) to  $m/z$  58 (CV), and thus it is likely that the effect described by the commenter is small. The differences in  $RIE_{SO4}$  may be more related to differences in background subtraction, as implied by the data shown in Fig. 11 (shown below), as discussed in that response. In short, since the background ("closed") signal decays faster in the CV, the difference signal that is used for AMS quantification (= open – closed) will be larger in the CV than the SV, even if the

intrinsic sensitivity to gas-phase sulfate decomposition products is the same. The background subtraction in the AMS is an example of a process that can significantly influence quantification, but is absent from the Murphy (2016a) model.



f) The concept of vaporization to multiple products followed by thermal decomposition is consistent with the observed pulse lengths. The concept could also possibly explain an otherwise puzzling observation about the RIE of ammonium nitrate. The RIE for ammonium has been reported to have a large range, 3.5 to 6.2 in the standard vaporizer and about 3 to >10 in the capture vaporizer [Jimenez et al., 2016, Crenn et al., 2015]. Multiple vaporization products followed by thermal decomposition would make the RIE more sensitive to details of the vaporization than simple evaporation to only  $\text{NH}_3(\text{g})$ .

Again we assume that the commenter is referring to the RIE of ammonium from ammonium nitrate, and not to the undefined “RIE of ammonium nitrate.” Note that  $\text{RIE}_{\text{NH}_4}$  can change due to variations on  $\text{IE}_{\text{NH}_4}$ , but also due to variations on  $\text{IE}_{\text{NO}_3}$  due to a variety of effects.

Vaporization/decomposition to multiple products is indeed consistent with the observed pulse lengths. However the observed pulse lengths do not appear to be consistent with a major fraction of the  $\text{NH}_x^+$  ions arising from ionization of  $\text{NH}_4\text{NO}_3(\text{g})$  and  $(\text{NH}_4)_2\text{SO}_4(\text{g})$  as previously published (see Figures 1e and 1f of Jimenez et al. (2016) and the associated discussion). This evidence has been briefly summarized in response to the next comment.

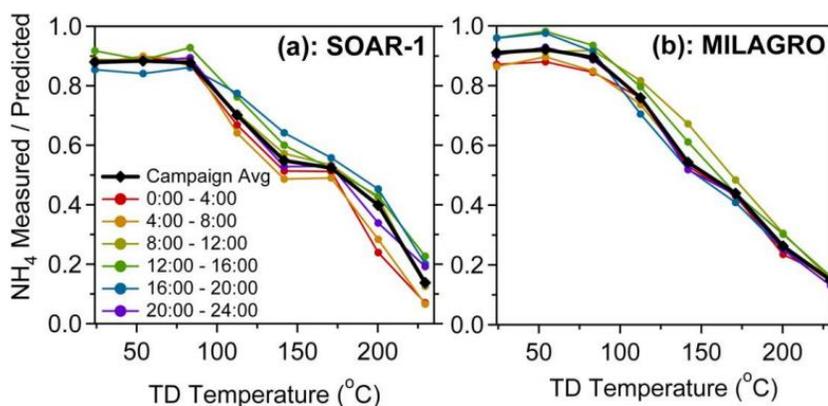
The new data in this manuscript make a very positive contribution to the understanding of the complicated vaporization of ammonium nitrate. The above hypotheses are consistent with the data but to confirm or falsify them would require data beyond the scope of this manuscript, such as a soft ionization technique.

We agree that data from a soft-ionization technique would be useful and we hope to secure funding for such experiments in the future. Here we conclude that the weight of the available evidence is against vaporization of molecular salts playing a major role in AMS detection:

### S1.2. Other evidence against the vaporization of a major fraction of $\text{NH}_4\text{NO}_3$ and $(\text{NH}_4)_2\text{SO}_4$ as intact salts in the AMS

The hypothesis of dominant vaporization of intact salts is also inconsistent with other published pieces of evidence discussed before, including:

(a) There is evidence from evaporation of ambient particles in thermal denuders that ammonia can evaporate from ammonium/nitrate/sulfate particles before the sulfate does, leaving the acids behind (Huffman et al., 2009, figure reproduced below as Fig. S5). It is thus plausible that the same process occurs in the AMS vaporizer, leading to very different fragmentation behavior of  $\text{NH}_3(\text{g})$  and the anions in the detection process (Fig. 4 in the main text).



**Fig. 5.**  $\text{NH}_4^+$  measured/predicted ratio (Eq. 1) shown as a function of TD temperature for averages of the total campaign (solid black line) and for six 4-h daily time blocks for (colored lines). Relative acidity increases as measured/predicted ratio decreases. (a) SOAR-1 and (b) MILAGRO.

Figure S5 This figure is reproduced from figure in Huffman et al. (2009)

(b) The constancy of the fragmentation pattern of  $\text{NH}_3(\text{g})$  across vaporizers and temperatures (compared to very large simultaneous changes for the associated anions), and

the high similarity with the NIST database pattern, also support separate vaporization of  $\text{NH}_3(\text{g})$ , as discussed in the main text.

(c) Single particle detection timescales for different ion fragments of the same species can provide insight into vaporization and ionization processes. The timescale of single particle signals of  $\text{NH}_4^+$  and the anion fragments is very different for both ammonium nitrate and ammonium sulfate (Jimenez et al., 2016). The fact that dominant cations and anions have different detection timescales indicates that they do not originate from the same species in the vapor phase.

(d) Ambient and laboratory data for mixed particles show that the sensitivity of ammonium relative to sulfate and nitrate is very constant (within 5%) over very wide changes in fractional composition, and also in the presence of large and variable amounts of internally-mixed organic species (Jimenez et al., 2016). If a very large fraction of the  $\text{NH}_x^+$  ions arose from the ionization of intact salt molecules and their subsequent fragmentation, it seems very unlikely that by coincidence the relative sensitivities to ammonium, nitrate, and sulfate would stay constant, despite order-of-magnitude changes in the relative composition of the vaporized salts, including likely vaporization of mixed salts. This evidence is especially important for ambient particles, which are often dominated by organic species.

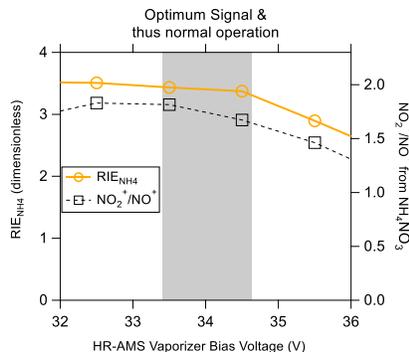
(e) The vaporization event lengths for single particles in the SV do not support the hypothesis (implicit in the calculations suggested by Murphy, 2017) that all species vaporize with the same temperature (either  $T_v$  or a lower value common for all vaporized species) (Jimenez et al., 2016). This is also consistent with the results of Saleh et al. (2017), who show that the expected vaporization temperatures in the AMS are lower than  $T_v$  due to evaporative cooling.

Although it is probably also beyond the scope of this manuscript, it would be helpful if the RIEs were shown as functions of the microchannel plate voltage and ion source parameters. If the RIEs are sensitive to the mass spectrometer parameters then that might provide an alternative explanation for the large ammonium RIE and its variability.

The ion source is always tuned for maximum signal and to avoid some known problems (e.g. very high  $K^+$ ,  $Na^+$  that are sometimes observed due to surface ionization), and it is not changed during instrument operation. Signals for species that are not formed by surface ionization do not depend strongly on small voltage changes around the optimum. The most sensitive tuning parameter is the vaporizer bias voltage (referred to as “heater bias” in AMS parlance). We have added the text shown below to the Supp. Info. in response to this request.

#### S1.4. Evidence against a strong effect of mass spectrometer tuning on $RIE_{NH_4}$

It is of interest to investigate whether a high sensitivity of AMS RIEs to mass spectrometer or MCP detector tuning parameters could provide an alternative explanation of the observed  $RIE_{NH_4}$  values. The most sensitive and important tuning voltage in the AMS is the vaporizer bias, which is tuned within a narrow signal maximum of  $\sim 1$  V. Figure S7 shows the variation of  $RIE_{NH_4}$  vs. vaporizer bias voltage while sampling pure  $NH_4NO_3$ .  $RIE_{NH_4}$  varies only by  $\sim 2\%$  over the optimum region, indicating that instrument tuning is unlikely to lead to substantial variations of  $RIE_{NH_4}$ .



**Figure S7. Variation of  $RIE_{NH_4}$  and the  $NO_2^+/NO^+$  ratio as a function of HR-AMS vaporizer bias voltage while sampling pure  $NH_4NO_3$  particles. Only  $\sim 2\%$  variation is observed for**

$RIE_{NH_4}$  across the optimum tuning region, while ~8% variation is observed for the  $NO_2^+/NO^+$  ratio.

The MCP detector voltage is always set high enough so that the overwhelming majority of the single ions are detected above the noise level, and it is not changed during instrument operation (other than to compensate for its degradation over time). Higher microchannel plate voltages would result on the same relative signals but shorter plate lifetime (and potentially saturation of the data acquisition card or MCP at very high instantaneous currents), while lower voltages would result in a well-known bias against weak signals (e.g. Hings et al., 2007). Thus, reporting RIE values vs. MCP voltage is not of high interest, as only one method for setting this voltage is used in practice.

Further changes to the text in response to the entire comment:

Summary of the discussion in the new Supp. Info section S1:

### S1.5. Summary

We conclude that the simple model of molecular flight and ionization proposed by Murphy (2016a) has difficulty explaining the observed high  $RIE_{NH_4}$  in the SV-AMS. While the processes included in the model are definitely occurring during AMS detection, this implies that other processes not accounted for in the model are also important. Evidence presented in this paper also suggests that detection in the CV-AMS detection may be closer to the Murphy (2016a) model, in particular since the observed  $T_v$ -dependence of some signals follows a similar trend as predicted by the model, vs. major differences for the SV-AMS (Jimenez et al., 2016). The key differences between the CV and SV detection are the suppression of particle bounce in the CV and the likelihood that vaporized molecules will undergo many collisions with the CV (vs. ~1 in the SV) and thus reach  $T_v$ . This suggests that those two processes may play an important role in explaining the discrepancies between the Murphy (2016a) model and experimental SV-AMS data: (a) particle bounce followed by slower evaporation from other surfaces in the detection region and/or (b) vaporization at temperatures lower than  $T_v$ , as expected from evaporative cooling (Saleh et al., 2017) and the lack of sufficient collisions between vaporized gas molecules and the SV

**for thermalization (Jimenez et al., 2016). However, we note that the high  $RI_{NH_4}$  in the CV-AMS still appears inconsistent with the simplified model. Further research, likely including the application of soft-ionization methods, is necessary to further clarify AMS detection details.**

We have revised the text at the end of the abstract to state:

**“We observe an extremely consistent fragmentation for ammonium, compared to very large changes for the associated anions. Together with other evidence, this indicates that it is unlikely that a major fraction of inorganic species vaporize as intact salts in the AMS.”**

And we have revised the text in the conclusions to state:

**“2) Multiple results support that it is unlikely that a dominant fraction of  $NH_4NO_3$ ,  $(NH_4)_2SO_4$  and  $NH_4Cl$  vaporize as intact molecular species, but rather they first decompose to  $NH_3(g)$  + acids (and other anion product species).**

## References

- Chien, W.-M., Chandra, D., Lau, K. H., Hildenbrand, D. L., and Helmy, A. M.: The vaporization of  $\text{NH}_4\text{NO}_3$ , *The Journal of Chemical Thermodynamics*, 42, 846-851, doi:10.1016/j.jct.2010.01.012, 2010.
- Crenn, V., Sciare, J., Croteau, P. L., Verlhac, S., Fröhlich, R., Belis, C. A., Aas, W., Äijälä, M., Alastuey, A., Artiñano, B., Baisnée, D., Bonnaire, N., Bressi, M., Canagaratna, M., Canonaco, F., Carbone, C., Cavalli, F., Coz, E., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Lunder, C., Minguillón, M. C., Močnik, G., O'Dowd, C. D., Ovadnevaite, J., Petit, J. E., Petralia, E., Poulain, L., Priestman, M., Riffault, V., Ripoll, A., Sarda-Estève, R., Slowik, J. G., Setyan, A., Wiedensohler, A., Baltensperger, U., Prévôt, A. S. H., Jayne, J. T., and Favez, O.: ACTRIS ACSM intercomparison – Part 1: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments, *Atmos. Meas. Tech.*, 8, 5063-5087, 10.5194/amt-8-5063-2015, 2015.
- DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory, *Aerosol Sci Tech*, 38, 1185-1205, Doi 10.1080/027868290903907, 2004.
- Drewnick, F., Diesch, J. M., Faber, P., and Borrmann, S.: Aerosol mass spectrometry: particle–vaporizer interactions and their consequences for the measurements, *Atmos. Meas. Tech.*, 8, 3811-3830, 10.5194/amt-8-3811-2015, 2015.
- Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, *P Natl Acad Sci USA*, 107, 6670-6675, DOI 10.1073/pnas.0912340107, 2010.
- Fry, J. L., Draper, D. C., Zarzana, K. J., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Brown, S. S., Cohen, R. C., Kaser, L., Hansel, A., Cappellin, L., Karl, T., Hodzic Roux, A., Turnipseed, A., Cantrell, C., Lefer, B. L., and Grossberg, N.: Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011, *Atmos. Chem. Phys.*, 13, 8585-8605, 10.5194/acp-13-8585-2013, 2013.
- Haynes, W.: *CRC Handbook of Chemistry and Physics* (96th ed.), CRC Press, 2015.
- Hings, S. S., Walter, S., Schneider, J., Borrmann, S., and Drewnick, F.: Comparison of a quadrupole and a time-of-flight aerosol mass spectrometer during the Feldberg aerosol characterization experiment 2004, *Aerosol Sci Tech*, 41, 679-691, Doi 10.1080/02786820701408483, 2007.
- Hogrefe, O., Drewnick, F., Lala, G. G., Schwab, J. J., and Demerjian, K. L.: Development, operation and applications of an aerosol generation, calibration and research facility, *Aerosol Sci Tech*, 38, 196-214, Doi 10.1080/02786820390229516, 2004.
- Hu, W., Campuzano-Jost, P., Day, D. A., Croteau, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Evaluation of the new capture vaporizer for aerosol mass spectrometers (AMS) through field studies of inorganic species, *Aerosol Sci Tech*, 0-0, 10.1080/02786826.2017.1296104, 2017a.
- Hu, W. W., Campuzano-Jost, P., Day, D. A., Croteau, P. L., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Evaluation of the new capture vaporizer for Aerosol Mass Spectrometers (AMS) through field studies of inorganic species, *Aerosol Sci Tech*, In press, 2017b.
- Huffman, J. A., Jayne, J. T., Drewnick, F., Aiken, A. C., Onasch, T., Worsnop, D. R., and Jimenez, J. L.: Design, modeling, optimization, and experimental tests of a particle beam width probe for the aerodyne aerosol mass spectrometer, *Aerosol Sci Tech*, 39, 1143-1163, Doi 10.1080/02786820500423782, 2005.

- Huffman, J. A., Docherty, K. S., Aiken, A. C., Cubison, M. J., Ulbrich, I. M., DeCarlo, P. F., Sueper, D., Jayne, J. T., Worsnop, D. R., Ziemann, P. J., and Jimenez, J. L.: Chemically-resolved aerosol volatility measurements from two megacity field studies, *Atmos Chem Phys*, 9, 7161-7182, 2009.
- Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R. C., Zhang, X. F., Smith, K. A., Morris, J. W., and Davidovits, P.: Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, *J Geophys Res-Atmos*, 108, 8425, Doi 10.1029/2001jd001213, 2003.
- Jimenez, J. L., Canagaratna, M. R., Drewnick, F., Allan, J. D., Alfarra, M. R., Middlebrook, A. M., Slowik, J. G., Zhang, Q., Coe, H., Jayne, J. T., and Worsnop, D. R.: Comment on “The effects of molecular weight and thermal decomposition on the sensitivity of a thermal desorption aerosol mass spectrometer”, *Aerosol Sci Tech*, 50, i-xv, 10.1080/02786826.2016.1205728, 2016.
- Linstrom, P. J., and Mallard, W. G.: NIST Chemistry WebBook, NIST Standard Reference Database Number 69, 2016.
- McLafferty, F. W., and Turecek, F.: Interpretation of mass spectra, University science books, 1993.
- Murphy, D.: Interactive comment on “Evaluation of the new capture vaporizer for Aerosol Mass Spectrometers (AMS) through laboratory studies of inorganic species” by Weiwei Hu et al., *Atmos. Meas. Tech. Discuss.*, <http://www.atmos-meas-tech-discuss.net/amt-2016-337/>, 2017.
- Murphy, D. M.: The effects of molecular weight and thermal decomposition on the sensitivity of a thermal desorption aerosol mass spectrometer, *Aerosol Sci Tech*, 50, 118-125, 10.1080/02786826.2015.1136403, 2016a.
- Murphy, D. M.: Reply to “Comment on the effects of molecular weight and thermal decomposition on the sensitivity of a thermal desorption aerosol mass spectrometer” by Jimenez et al, *Aerosol Sci Tech*, 1-7, 10.1080/02786826.2016.1254347, 2016b.
- Pieber, S. M., El Haddad, I., Slowik, J. G., Canagaratna, M. R., Jayne, J. T., Platt, S. M., Bozzetti, C., Daellenbach, K. R., Fröhlich, R., Vlachou, A., Klein, F., Dommen, J., Miljevic, B., Jiménez, J. L., Worsnop, D. R., Baltensperger, U., and Prévôt, A. S. H.: Inorganic Salt Interference on CO<sub>2</sub>+ in Aerodyne AMS and ACSM Organic Aerosol Composition Studies, *Environ Sci Technol*, 50, 10494–10503, 10.1021/acs.est.6b01035, 2016.
- Robinson, E. S., Onasch, T. B., Worsnop, D., and Donahue, N. M.: Collection efficiency of a-pinene secondary organic aerosol particles explored via light scattering single particle aerosol mass spectrometry, *Atmos. Meas. Tech. Discuss.*, 2016, 1-29, 10.5194/amt-2016-271, 2017.
- Salcedo, D., Onasch, T. B., Dzepina, K., Canagaratna, M. R., Zhang, Q., Huffman, J. A., DeCarlo, P. F., Jayne, J. T., Mortimer, P., Worsnop, D. R., Kolb, C. E., Johnson, K. S., Zuberi, B., Marr, L. C., Volkamer, R., Molina, L. T., Molina, M. J., Cardenas, B., Bernabe, R. M., Marquez, C., Gaffney, J. S., Marley, N. A., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Leshner, R., Shirley, T., and Jimenez, J. L.: Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite, *Atmos Chem Phys*, 6, 925-946, 2006.
- Saleh, R., Robinson, E. S., Ahern, A. T., and Donahue, N. M.: Evaporation rate of particles in the vaporizer of the Aerodyne aerosol mass spectrometer, *Aerosol Sci Tech*, 1-8, 10.1080/02786826.2016.1271109, 2017.
- Xu, L., Suresh, S., Guo, H., Weber, R. J., and Ng, N. L.: Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates, *Atmos. Chem. Phys.*, 15, 7307-7336, 10.5194/acp-15-7307-2015, 2015.
- Xu, W., Croteau, P., Williams, L., Canagaratna, M., Onasch, T., Cross, E., Zhang, X., Robinson, W., Worsnop, D., and Jayne, J.: Laboratory characterization of an aerosol chemical speciation monitor with PM<sub>2.5</sub> measurement capability, *Aerosol Sci Tech*, 1-15, 10.1080/02786826.2016.1241859, 2017.

