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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.

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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 NH3(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:

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,

$NH_4NO_3(s) \rightarrow a \times NH_3(g) + b \times HNO_3(g) + c \times NO_2(g) + d \times NO(g) + \text{others}$ [1]

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 $NH_3(g)$ (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.

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.

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.

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.

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 NH3(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:

a) Ammonium nitrate has been observed to vaporize in vacuum to a combination of NH3(g), HNO3(g), and NH4NO3(g) [Chien et al., 2010]. We assume that those products also apply to the vaporization conditions present in the AMS.

b) There is thermal decomposition on the hot surfaces of the vaporizers. Thus, there will be less HNO3(g) and NH4NO3(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 NH4NO3(g) effusing from the vaporizer at about 80 C, so decomposition does not occur on every wall collision.

c) We assume that NH4NO3(g) fragments in an electron beam to produce a significant fraction of NHx+ ions, producing a high RIE for the portion of NH4NO3(g) that survives the vaporizer.

d) For the capture vaporizer, the data in Figure 3 suggest that much of the nitrate thermally decomposes to NO(g). If only NO(g) and NH3(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 NH4NO3(g) and some mass discrimination.

e) For the standard vaporizer, the data in Figure 3 suggest that much of the nitrate ends up as NO2(g) and HNO3(g). The calculated RIE for NH3(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 NH4NO3(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, NO(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 NH4NO3(g) (or similar molecule) is contributing to the NHx+ signal, leading to a large numerator.

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 NH3(g).

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. 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.

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Discussion paper