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Evaluation of the new capture vapourizer for aerosol mass spectrometers (AMS) through laboratory studies of inorganic species

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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 RIE_{NH4} are difficult to reconcile with this simple model (Jimenez et al., 2016). To explain this discrepancy, it has been proposed that NH_4NO_3 and $(NH_4)_2SO_4$ vaporize as intact salts in the AMS (Murphy, 2016a; Murphy, 2017). The present study allows some additional considerations to be made on this topic.

S1.1. Quantitative analysis of RIE_{NH4} when a fraction of NH_4NO_3 vaporizes as an intact salt

It has been suggested that the high RIE_{NH4} observed in the AMS can be explained by the vaporization of intact NH_4NO_3 molecules, followed by their ionization, and production of NH_3^+ ions with high efficiency from that process (Murphy, 2017). However, it is very difficult to reach a typical RIE_{NH4} of 4 based on this hypothesis with reasonable assumptions. This is even more so when considering values of RIE_{NH4} ~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 RIE_{NH4} 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 600ºC, which is much larger than the 64-92ºC used in those experiments:
    a. NH_4NO_3 → 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. ½ of the H_xNO_y(g) is NO_2(g) and the other ½ 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.:

$$NH_4NO_3^+ \rightarrow 50\%\ NH_3^+ + 50\%\ HNO_3(g) + 50\%\ NH_3(g) + 50\%\ HNO_3^+$$

With those assumptions $RIE_{NH4} \sim 1.1$. If one assumes in (d) 100% of either $NO_2(g)$ or $HNO_3(g)$ for $H_xNO_y^+(g)$, then $RIE_{NH4} \sim 1.05$-1.12 can be obtained. If one assumes in (e) that the fragmentation of $NH_4NO_3^+$ yields 75% NH_x^+, $RIE_{NH4} = 1.5$ (if one assumes 100% NH_x^+, then $RIE_{NH4} = 2.1$). Thus even with aggressive assumptions, the hypothesis is not consistent with the observed RIE_{NH4} 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°C higher T_v), probably near zero. If we assume a value of 5%, and the rest of the default assumptions above, then $RIE_{NH4} \sim 0.7$. Thus it seems very difficult to quantitatively explain the observed RIE_{NH4} 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°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.

S1.2. Other evidence against the vaporization of a major fraction of NH_4NO_3 and $(NH_4)_2SO_4$ 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 $NH_3(g)$ and the anions in the detection process (Fig. 4 in the main text).

(b) The constancy of the fragmentation pattern of $NH_3(g)$ 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 NH_3(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 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 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.

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 NH_x^+ ions formed from ammonium were detected more efficiently than the NO_x^+ (and SO_x^+) ions, that effect could contribute to a larger-than-expected RIE_{NH4}. 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 N_2 and 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 C^+/CO_2^+ ratios from CO_2(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 NH_4NO_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 NH_x^+ ions is ~5% (10%) larger than for NO_x^+ (SO_x^+) ions, and thus it is a very small effect that can only contribute little to the high observed RIE_{NH4}.

S1.4. Evidence against a strong effect of mass spectrometer tuning on RIE_{NH4}

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_{NH4} values. The most sensitive and important tuning voltage in the AMS is the vaporizer bias, which is tuned within a narrow signal maximum of ~ 1 V. Figure S7 shows the variation of RIE_{NH4} vs. vaporizer bias voltage while sampling pure NH_4NO_3. RIE_{NH4} varies only by ~2% over the optimum region, indicating that instrument tuning is unlikely to lead to substantial variations of RIE_{NH4}.

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.

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_{NH4} 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 RIE_{NH4} 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.

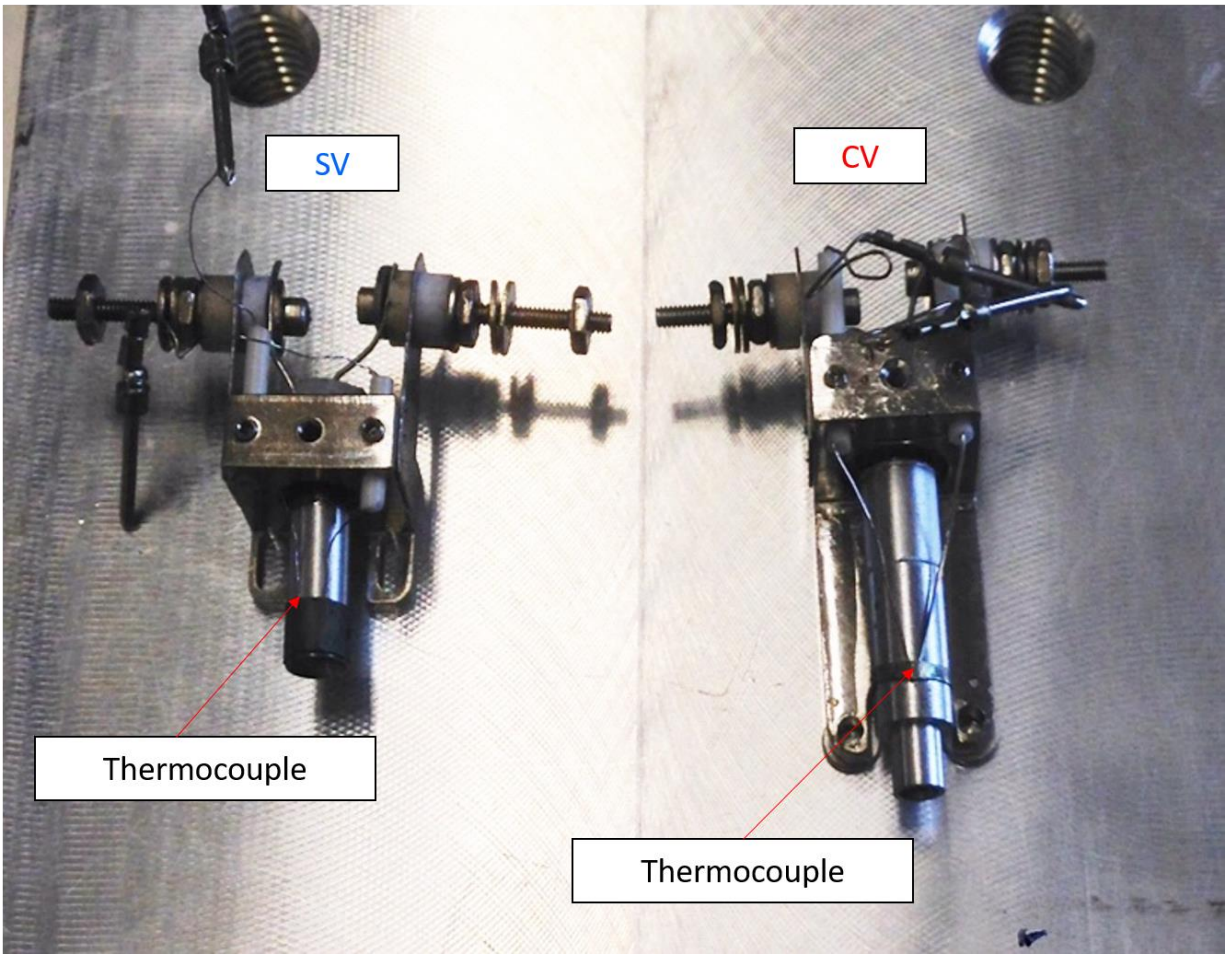

Figure S1 Picture of a standard vaporizer (SV, left) and a capture vaporizer (CV, right).

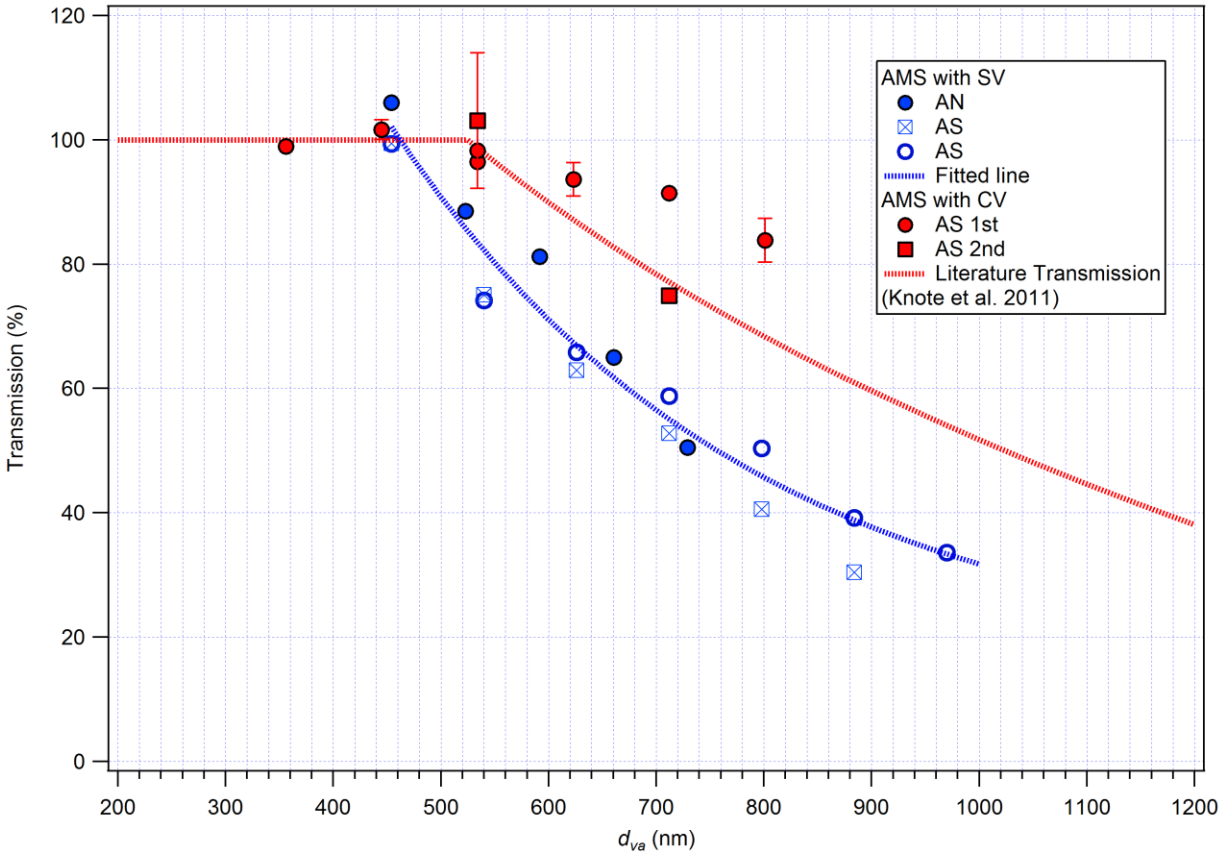

Figure S2 Lens transmission curve measured in this study for the AMSs with CV and SV. For d_{va} below 460 nm in SV AMS and 550 nm in CV AMS, no lens transmission correction was needed (E_L=1). In the experiments shown in this study, only $NaNO_3$ needs a transition loss correction for its high d_{va} (=680nm). During the experiment, an underperforming lens (that has since been replaced) was used in AMS with SV, thus showed a larger particle loss than the AMS with CV at high d_{va}. Normally, lens transmission curve is similar to that from CV AMS in this study, however individual AMS lens transmission calibrations are always recommended.

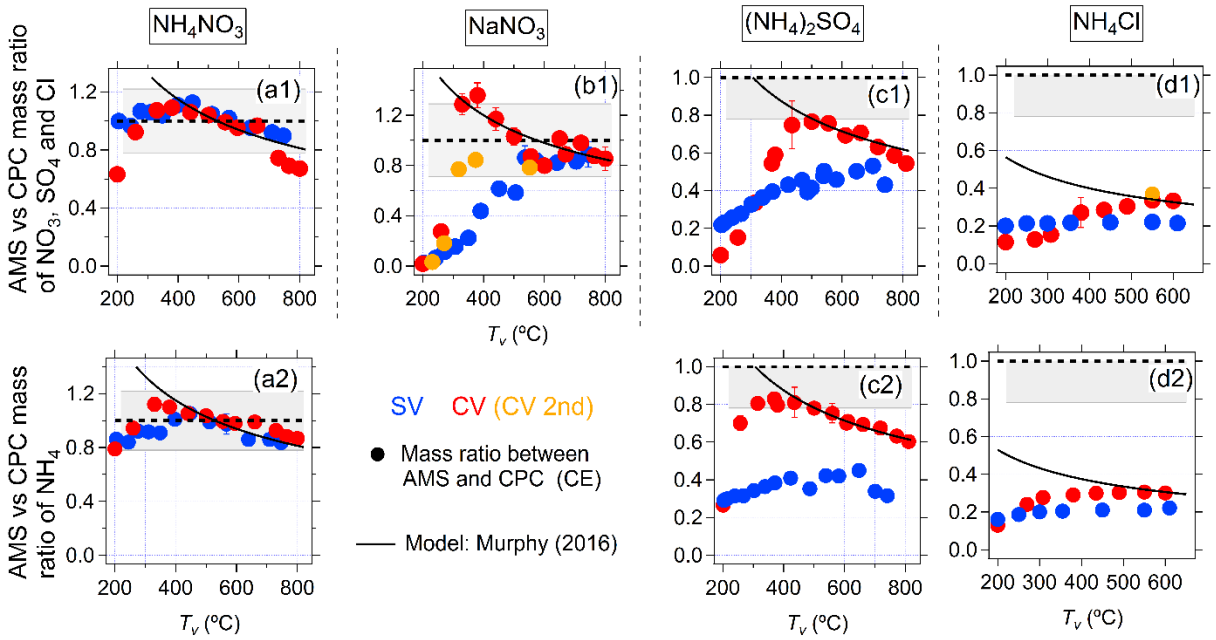

Figure S3 Ratios of mass concentration between AMS and CPC measurements (CE) from four inorganic species (dried monodisperse particles) of (a) 300 nm NH_4NO_3; (b) 250 nm $(NH_4)_2SO_4$; (c) 300 nm $NaNO_3$; (d) 300 nm NH_4Cl. The black line was calculated based the relationship described in Eq. (2) 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 ℃. 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).

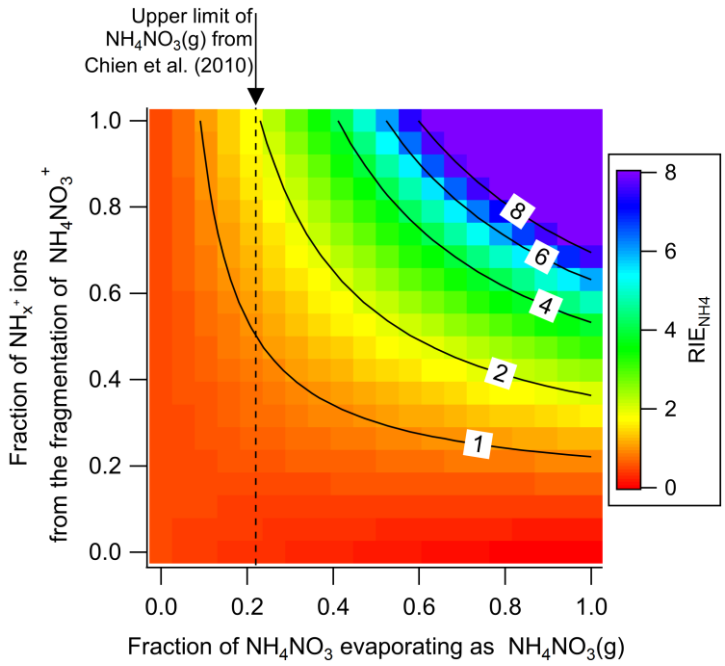

Figure S4 Estimated RIE_{NH4} as a function of the assumed fraction of NH_4NO_3 vaporizing as $NH_4NO_3(g)$, and the fraction of NH_x^+ ions formed from the fragmentation of $NH_4NO_3^+$. Also marked is the upper limit fraction of $NH_4NO_3(g)$ evaporated at ~80^{o}C (Chien et al., 2010)

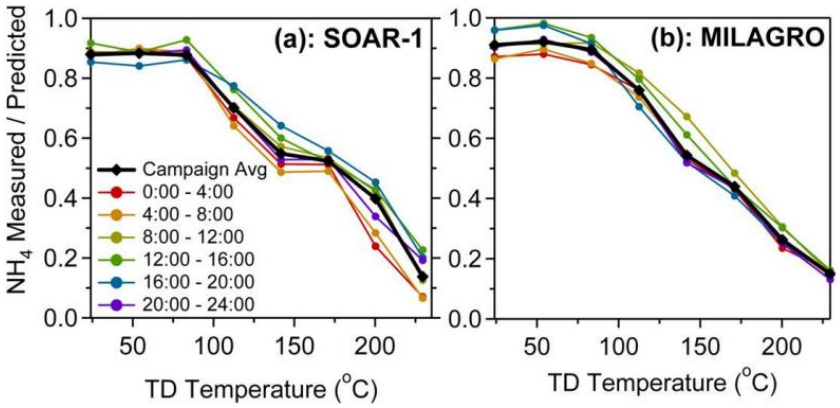

Fig. 5. NH_4^+ measured/predicted ratio (Eq. 1) shown as a function of TD temperature for averages of the total campaign (solid black line) and for six 4-h daily time blocks for (colored lines). Relative acidity increases as measured/predicted ratio decreases. **(a)** SOAR-1 and **(b)** MILAGRO.

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

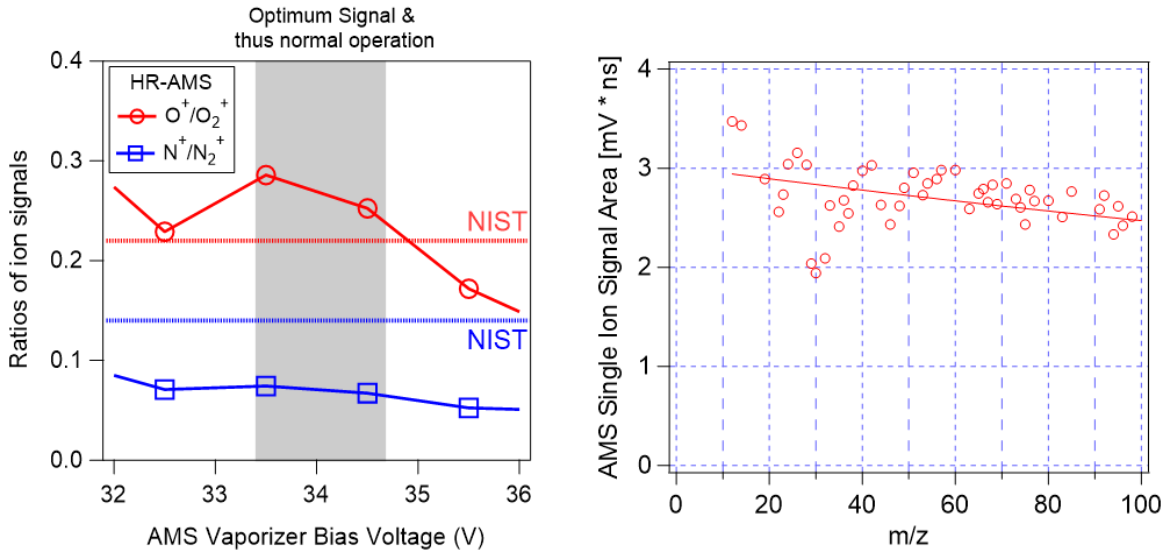

Figure S6 Left: comparison of the fragmentation patterns of O_2 and N_2 in the HR-AMS to those in the NIST database. Right: measured response of the AMS microchannel plate to single ions as a function of *m/z*. Only *m/z* at which the signal is dominated by individual ions events, based on ion detection frequencies while analyzing the AMS background signal, are shown.

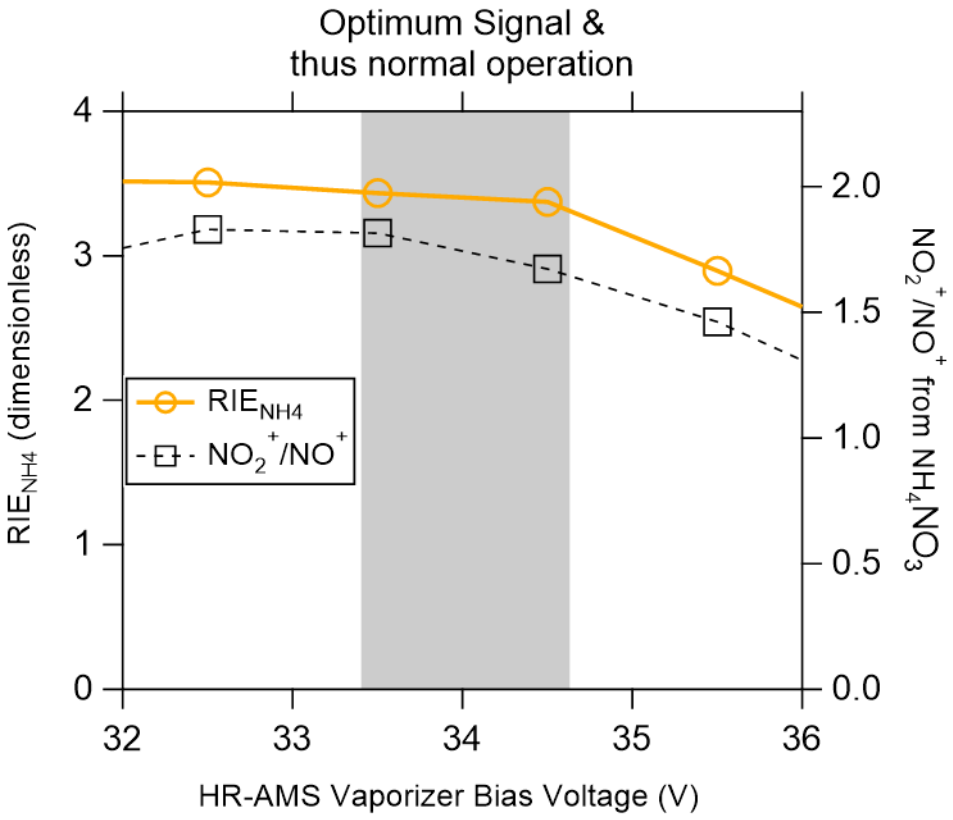

Figure S7 Variation of RIE_{NH4} and the NO_2^+/NO^+ ratio as a function of HR-AMS vaporizer bias voltage while sampling pure NH_4NO_3 particles. Only ~2% variation is observed for RIE_{NH4} across the optimum tuning region, while ~8% variation is observed for the NO_2^+/NO^+ ratio.

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