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Weiwei Hu  
*University of Colorado Boulder*

Pedro Campuzano-Jost  
*University of Colorado Boulder*

Douglas A. Day  
*University of Colorado Boulder*

Philip Croteau  
*Aerodyne Research, Inc.*

Manjula R. Canagaratna  
*Aerodyne Research, Inc.*

*See next page for additional authors*

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

Weiwei Hu1,2, Pedro Campuzano-Jost1,2, Douglas A. Day1,2, Philip Croteau3, Manjula R. Canagaratna3, John T. Jayne3, Douglas R. Worsnop3, and Jose L. Jimenez1,2

1Cooperative Institute for Research in the Environmental Sciences (CIRES), University of Colorado at Boulder, 216 UCB, Boulder, CO 80309, USA
2Department of Chemistry & Biochemistry, University of Colorado at Boulder, 216 UCB, Boulder, CO 80309, USA
3Aerodyne Research, Inc., Billerica, Massachusetts, USA

Correspondence to: Jose L. Jimenez (jose.jimenez@colorado.edu)

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Abstract. Aerosol mass spectrometers (AMSs) and Aerosol Chemical Speciation Monitors (ACSMs) commercialized by Aerodyne are widely used to measure the non-refractory species in submicron particles. With the standard vapourizer (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. A new capture vapourizer (CV) has been designed to reduce the need for a bounce-related CE correction.

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, NH₄NO₃, NaNO₃, (NH₄)₂SO₄ and NH₄Cl, which typically constitute the majority of the mass of ambient submicron inorganic species, are studied. The effect of vapourizer temperature (Tv ∼ 200–800 °C) on the detected fragments, CE and size distributions are investigated. A TV of 500–550 °C for the CV is recommended. In the CV, CE was identical (around unity) for more volatile species (e.g. NH₄NO₃) and comparable to or higher than the SV for less-volatile species (e.g. (NH₄)₂SO₄), demonstrating an improvement in CE for laboratory inorganic species in the CV. The detected relative intensities of fragments of NO₃ and SO₄ species observed with the CV are different from those observed with the SV, and are consistent with additional thermal decomposition arising from the increased residence time and multiple collisions. Increased residence times with the CV also lead to broader 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 CO₂(g) from sampled nitrate on the vapourizer surface, which has been reported for the SV, is negligible for the CV for NH₄NO₃ and comparable to the SV for NaNO₃. 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 vapourizes as intact salts in the AMS.

1 Introduction

Submicron aerosols have major effects on climate and human health (Hallquist et al., 2009; Heal et al., 2012; IPCC, 2013; Fuzzi et al., 2015). In recent decades, various new instruments have been developed to measure different properties of fine aerosols (Turpin et al., 2000; Farmer and Jimenez, 2010). Among them, Aerodyne aerosol mass spectrometers (AMS, produced by Aerodyne Research Inc., Billerica, MA, USA) have emerged as one of the most commonly used online aerosol composition instruments due to their fast response (~ seconds to minutes) and ability to quantify the bulk chemical composition and size distribution of submicron non-refractory aerosols, i.e. organic aerosol, sulfate, ammonium,
Comparisons between AMS and other co-located aerosol instruments in various field studies (Drewnick et al., 2003, 2004b; Allan et al., 2004a; Takegawa et al., 2009; Docherty et al., 2011; Middlebrook et al., 2012) or laboratory studies (Bahreini et al., 2005; Matthew et al., 2008; Docherty et al., 2012) have shown that, despite the typically strong correlation between AMS and other aerosol instrument measurements, a correction factor needs to be used for mass quantification in the AMS. This factor is known to be due predominately to the AMS collection efficiency (CE), which is the ratio between the concentration of particles detected in AMS and the concentration of particles introduced to the AMS inlet (Huffman et al., 2005; Matthew et al., 2008). CE < 1 in the AMS can be due to particle loss within the (1) aerodynamic lens ($E_L$), depending on particle size, lens design and pressure (Jayne et al., 2000; Liu et al., 2007; Bahreini et al., 2008); (2) particle time-of-flight (PToF) chamber ($E_S$) caused by non-spherical particles that result in broader particle beams with some particles not reaching the vapourizer (Huffman et al., 2005; Salecedo et al., 2007), or (3) particle bounce on the vapourizer ($E_B$). The final CE is the product of these three factors ($CE = E_L \times E_S \times E_B$) (Huffman et al., 2005). Multiple laboratory and field measurements have shown that $E_L$ and $E_S$ are typically near unity for submicron particles, whereas $E_B$ is the dominant term (Matthew et al., 2008; Middlebrook et al., 2012). All AMS commercial instruments to date have used a standard vapourizer (SV), shaped as an inverted cone of porous tungsten, and kept at vapourizer temperature ($T_v$) of $\sim 550–600 ^\circ C$ for ambient measurements (and most laboratory measurements).

Various factors, including RH in the sampling line, aerosol water content, aerosol acidity-neutralization of sulfate content and ammonium nitrate fraction in total aerosol, can influence CE, and thus aerosol quantification in the AMS (Quinn et al., 2006; Middlebrook et al., 2012). CE in the SV is in the range 0.2–0.4 for pure ammonium sulfate (Drewnick et al., 2004a; Weimer et al., 2006; Takegawa et al., 2009) and $\sim 1$ for pure ammonium nitrate (Jayne et al., 2000; Middlebrook et al., 2012). A parameterization of CE for ambient particles based on composition has been used successfully in many environments (Middlebrook et al., 2012), but the remaining uncertainties on CE are thought to dominate the uncertainty of AMS concentration measurements (Bahreini et al., 2009).

Efforts aiming to minimize the uncertainty of aerosol mass spectrometers have been conducted recently. Using the differential mobility analyser (DMA) coupled to an impactor to quantify the particle bounce fraction, Kang et al. (2015) tested different metal materials, vapourizer porosities and shapes for particle bouncing and found copper, meshed/porous surface, as well as reversed T-shape materials best at reducing the particle bounce fraction. Each version can reduce the bounce fraction by around 10–50 % compared to the basic set up, indicating that CE can be improved through vapourizer design. A custom instrument similar to the AMS has a different design of particle trap/vapourizer to increase CE (Takegawa et al., 2012; Ozawa et al., 2016). A regression slope of 0.7 for sulfate, probably caused by different size cuts in a field study, was observed between this and other instruments.

A capture vapourizer (CV) has been recently developed by Aerodyne (Jayne and Worsnop, 2016) to achieve CE = 1 for ambient particles in the AMS; hence it decrease the quantification uncertainty (Xu et al., 2017). We have performed laboratory studies to evaluate the performance and detection characteristics of the CV for key inorganic species, i.e. NH$_4$NO$_3$, NaNO$_3$, (NH$_4$)$_2$SO$_4$ and NH$_4$Cl. We compare fragmentation patterns, CE and particle size distributions as a function of $T_v$ (200–800 °C) in both the SV and CV. This is the first time that the performance of laboratory-generated inorganic aerosol in AMS with the SV and CV over a wide range of $T_v$ (200–800°C) has been reported. Recommendations for optimal $T_v$ and fragmentation table modifications for the CV are given. Fragmentation and quantification of NH$_4$NO$_3$ as a function of particle beam position on the vapourizers is also investigated. Pieber et al. (2016) recently showed that inorganic salts can produce CO$_2$(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.

2 Experimental set-up and instrumentation

2.1 Brief description of the capture vapourizer

The detailed design of the CV has been presented in Xu et al. (2017); thus only a brief description is provided here. Both the SV and CV are based on cartridge heaters, which are resistively heated by passing power through a $\sim 0.1$ mm diameter coiled tungsten wire positioned inside of the tube (Jayne et al., 2000; Canagaratna et al., 2007; Xu et al., 2017). The CV tube length is about double that of the SV (Fig. S1 in the Supplement). The particle impact surface of the SV is an inverted cone, whereas the CV is designed to have a cage inside the vapourizer with a narrow entrance (Fig. 1a) to minimize particle bouncing loss. The SV is constructed from 80 % dense porous tungsten, while the CV is solid molybdenum.

2.2 Laboratory measurement set-up

Laboratory experiments in this study were set up as shown in Fig. 1b. Pure inorganic salt particles were generated with a Collison atomizer (model: 3076; TSI, US) from their dilute water solutions. Atomized particles were dried with a Nafion (MD-110-24S-4, Perma Pure LCC, US) or a silica gel diffusion dryer (RH < 30 %), and then were size selected by a differential mobility analyser (DMA, model: 3080, TSI, US). To remove multiple charged particles (required for accu-
rate quantification), impactors with different sizes (i.e. 0.071, 0.0508 or 0.0457 cm for 0.6–0.75 L min\(^{-1}\) aerosol sampling flow) were used upstream of the DMA. The particle cut sizes of those impactors varied with flow rate and particle properties, which can be calculated using Aerosol Instrument Manager (AIM) from TSI. The mass-based size distribution from SV suggested the doubly charged particle mass fractions are less than 10 % in all cases (Sect. 3.3, Figs. 12–13). Finally, the monodisperse particles were measured by two nominally identical high-resolution time-of-flight AMS (HR-ToF-AMS) equipped with the SV and CV respectively. Particle number concentration was determined with a condensation particle counter (CPC, model: 3760 or 3010, TSI, US) sampling in parallel to the AMSs. The mass concentrations can be calculated from the CPC and size data.

The volume flow rate into the AMS was ∼0.1 L min\(^{-1}\). A bypass flow (0.2–0.3 L min\(^{-1}\)) near the inlet of each AMS was added to reduce time in the tubing and thus reduce particle losses. Sampling tubes were usually copper or stainless steel with 1/4 inch outer diameter. All of the standard inorganic chemical compounds used in this study were analytical grade (purity > 99.9 %). Water used was either NERL reagent grade water from Thermo Scientific Inc. (USA) or milli-Q water purified by a Milli-Q Integral Water Purification System (EMD Millipore Corporation, Germany).

2.3 AMS measurements

In this study, most of the comparison experiments were conducted using HR-ToF-AMSs (DeCarlo et al., 2006). The one exception was the lens alignment experiment for the SV, which was carried out in a quadrupole AMS (Q-AMS, Jayne et al., 2000). All the instruments used for these experiments have the same chamber length (chopper to vapourizer distance: 295 mm), while the Q-AMS had a longer chamber (395 mm). ToF-AMS data were analysed with the standard software packages (Squirrel version ≥ 1.52 M and PIKA version ≥ 1.12). The Q-AMS data were analysed with the Q-AMS analysis toolkit (version 1.43). All the ToF MS mode data used in this study were high-resolution (HR) data, and PToF data were unit mass resolution (UMR) data.

Before each set of experiments, a lens alignment was performed on each AMS. Mass concentrations of detected aerosols were obtained from the MS-mode signal, which is the difference in signal between chopper blocking and not blocking the particle beam: beam open (6 or 5 s) minus beam closed (4 or 5 s) (Jimenez et al., 2003). The ionization and detection efficiency (IE) of nitrate and the relative ionization efficiency (RIE) of ammonium were calibrated with dry monodisperse 400 nm ammonium nitrate (NH\(_4\)NO\(_3\)) particles every few days during the laboratory studies (Canagaratna et al., 2007). Both BFSP (brute-force single particle mode; DeCarlo et al., 2006) and methods based on CPC measurements (described above) were applied to the SV AMS, while only the latter method was applied to the CV AMS.

It is not possible to apply the BFSP method to the CV AMS due to the longer residence time of vapourized molecules in the CV resulting in a broadening of single-particle pulse so that their signal cannot be sufficiently discriminated from the noise, at least for particles of sizes that have 90 % transmission into the AMS (400 nm NH\(_4\)NO\(_3\)). The escape time of NH\(_4\)NO\(_3\) vapours from the CV is larger than 200 µs (see Sect. 3.1.4), which is much longer than the measured duration of single particle events of NH\(_4\)NO\(_3\) in the SV of ∼25–40 µs (Drewnick et al., 2015). For other species such as (NH\(_4\))\(_2\)SO\(_4\), an additional cause of broad-
ening is due to additional particle collisions inside the CV after an initial bounce event.

Most IE calibrations in AMS were carried out simultaneously for both AMSs using the same stream of calibrated particles. Sulfate RIE (RIE SO4) was calibrated with pure ammonium sulfate ((NH4)2SO4) by measuring the relative response of ammonium in both NH3NO3 and (NH4)2SO4, Tv in the range of 200–800 °C were used in both AMSs to investigate the influences of this parameter. Chloride RIE applied in this study is 1.3.

2.4 Determination of vapourizer temperature (Tv)

Tv is a function of the electrical power (voltage × current) supplied to the vapourizer, and is controlled by the electronics box (EBOX) in the AMS. Tv can be quantified in two ways. One method is through a thermocouple attached to the vapourizer body. The relationship between the thermocouple reading and the applied vapourizer power for the SV and CV is shown in Fig. 2a. The curve for the SV was obtained based on a combination of thermocouple-power readings from several different AMSs (Williams, 2010). The thermocouple reading vs. vapourizer power results for the CV in our AMS were similar to those for the SV when vapourizer power was below 2 watts. However, it was lower when vapourizer power was between 2 and 10 watts. Since the thermocouples were mounted outside the vapourizer body (Figs. 1a and S1) in both vapourizers, neither thermocouple measured the actual surface Tv that the particles encountered but the measured temperature is assumed to be reasonably close. The thermocouple reading method usually works well for newly installed vapourizers. However, with vapourizer aging, the thermocouple often becomes detached and hence reports a lower Tv reading than the true values (Williams, 2010). The input vapourizer power, on the other hand, is likely to be more reliable than the thermocouple reading in most of the conditions.

Thus, an alternative method to determine Tv without the thermocouple can be useful. Williams (2010) reported that the measured size distribution width (quantified as the full width at half maximum, FWHM) of the NO3 signal from monodisperse NaNO3 particles starts to broaden at Tv below 600 °C (±50 °C) for SV. The Tv broadening is defined as the point at which the size distribution width increases above 20 % of the lowest peak width, which was determined by averaging peak width values when vapourizer power is above 4.5 W. This broadening was repeatable in different AMS systems and was proposed as a technique to verify Tv settings. This method is expected to allow identification of problems with the thermocouple measurement, since it directly reflects the chemical vapourization properties of a standard compound. In this study, size distributions of monodisperse 300 nm NaNO3 particles were measured at different Tv (300–800 °C) multiple times (2014–2016). A summary of those results for NaNO3 size distributions of FWHM as a function of vapourizer power is displayed in Fig. 2b. The FWHM of NaNO3 for the SV in our AMS was consistent with results from Williams (2010). In the 2014 measurements, the broadening threshold temperature of the SV corresponded to a higher nominal vapourizer power than the others. It was found that the AMS electronic box (AMS EBOX) at that time was delivering less power to vapourizer than the readout indicated. Thus, the Tv was corrected by matching the 2014 curve to the others from SV, was applied. The yellow background shows the range of vapourizer power between 3.6 and 4 W, where a transition in the detected peak width occurs in both vapourizers. The blue and pink dashed lines are the average values of peak width from CU 2016 curves of SV and CV (respectively) when vapourizer power is above 4.5 W.
2.5 SMPS measurements

SMPS particle sizing was verified with monodisperse polystyrene latex spheres (PSLs) (Duke Scientific, Palo Alto, CA, US) with diameters of 250–400 nm. The SMPS sheath and sample flow rates were calibrated before each set of experiments. Mass concentrations were calculated by multiplying reported volume concentrations with their corresponding densities. The densities used for NH$_4$NO$_3$, NaNO$_3$, (NH$_4$)$_2$SO$_4$ and NH$_4$Cl in this study are 1.72, 2.26, 1.78 and 1.52 g cm$^{-3}$ respectively (Haynes, 2015). A Jayne shape factor of 0.8 was applied to NH$_4$NO$_3$. This Jayne shape factor was experimentally determined by comparing the mobility and vacuum aerodynamic diameters ($d_{va}$) measured for NH$_4$NO$_3$ (Jayne et al., 2000; DeCarlo et al., 2004) and used to correct for the fact that the effective density of pure NH$_4$NO$_3$ particles is less than the bulk density. Possible reasons for this lower effectiveness than bulk density include particle non-sphericity or the formation of a phase of lower density for the aerosols compared to macroscopic NH$_4$NO$_3$ (DeCarlo et al., 2004). Experimental investigation of the fundamental reasons for the lower effective density of NH$_4$NO$_3$ compared to the bulk species is recommended.

3 Results and discussion

3.1 Thermal decomposition and fragmentation of standard species

3.1.1 Nitrate and sulfate fragmentation patterns

The fragment ion comparisons of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ particles in an argon flow (to remove interfering ions from air) between the SV and CV for $T_v \approx 500–550 ^\circ$C are shown in Table 1. A slightly lower $T_v$ than the standard 600 $^\circ$C used in the SV was chosen here. This is because lower $T_v$ is recommended for a general CV operation, as discussed below in Sect. 3.3.2. The major ions of nitrate in NH$_4$NO$_3$ are NO$^+$ and NO$_2^+$, comprising of $\sim$98% of the signal in the SV and 99% in the CV (Table 1, Jayne et al., 2000; Allan et al., 2004b; Hogrefe et al., 2004). NO$_2^+$ and NO$^+$ showed strong linear correlations across a wide range of NH$_4$NO$_3$ mass concentrations, as expected (Fig. 3a). The ratio of NO$_2^+$ / NO$^+$ of NH$_4$NO$_3$ in SV was $\sim 0.35$ within the range of NO$_2^+$ / NO$^+$ ratios reported in other studies (0.29–0.75) (Hogrefe et al., 2004; Bae et al., 2007; Farmer and Jimenez, 2010; Fry et al., 2013). In contrast, in the CV it was only 0.04–0.07, an order of magnitude lower. The much lower NO$_2^+$ / NO$^+$ ratios in the CV than in the SV are consistent with results of Xu et al. (2017). To qualitatively interpret this difference, a possible mechanism of NO$_2^+$ and NO$^+$ production in the AMS system is discussed.

Nitrate from NH$_4$NO$_3$ particles can produce gas-phase HNO$_3$(g), NO$_2$(g) and NO(g) species (Drewnick et al., 2015), as

\[
\text{NH}_4\text{NO}_3(s) \rightarrow a \times \text{NH}_3(g) + b \times \text{HNO}_3(g) + c \times \text{NO}_2(g) + d \times \text{NO}(g) + \text{others.}
\]  

The electron ionization (EI) fragmentation products of HNO$_3$(g) and NO$_2$(g) at 70 eV are mostly NO$^+$ and NO$_2^+$, with NO$_2^+$ / NO$^+$ ratios of $\sim 1.17–2$ and 0.3–0.5 respectively (Friedel et al., 1959; Linstrom and Mallard, 2016). NO(g) produces almost only NO$^+$, and no NO$_2^+$ (Linstrom and Mallard, 2016). In the AMS (with SV) the fragments observed are often smaller due to thermal decomposition and fragmentation of hotter ions, given the higher temperatures of the neutrals compared to NIST (National Institute of Standards and Technology; Canagaratna et al., 2015). Taking the NIST ratios as upper limits, the NO$_2^+$ / NO$^+$ ratio in the SV (0.29–0.75) might result from a combination of EI ionization from HNO$_3$(g), NO$_2$(g) and NO(g). Pieber et al. (2016) speculated that the NO$_2$(g) is an important thermal decomposition product for NH$_4$NO$_3$ in SV. The NO$_2^+$ / NO$^+$ ratio in the CV (0.04–0.07) was much less than the NIST ratios from NO$_2$(g) and HNO$_3$(g) (0.3–2), suggesting that the ionization of NO(g) is likely the major pathway for the CV. The dominance of NO(g) in the CV may be due to the longer residence time and increased number of collisions of vapours in the CV, leading to enhanced thermal decomposition. Indeed, NO(g) is also the favoured thermodynamic product for $T_v$ of $\sim 500–650 ^\circ$C (Wang et al., 2015).

A shift to smaller molecular weight ion fragments for the CV was observed for (NH$_4$)$_2$SO$_4$ as well (Fig. 3b). The thermal decomposition products of (NH$_4$)$_2$SO$_4$ are shown below:

\[
(\text{NH}_4)_2\text{SO}_4(s) \rightarrow a \times \text{NH}_3(g) + b \times \text{H}_2\text{SO}_4(g) + c \times \text{SO}_3(g) + d \times \text{SO}_2(g) + e \times \text{H}_2\text{O} + \text{others.}
\]  

The major ions from sulfate aerosols in the AMS are SO$^+$, SO$_2^+$, SO$_3^+$, HSO$_3^+$ and H$_2$SO$_4^+$ (Allan et al., 2004b; Hogrefe et al., 2004). Ratios of SO$_3^+$, HSO$_3^+$ and H$_2$SO$_4^+$ to SO$^+$ signal in the CV ($< 0.05$) were consistently lower than for SV (0.11–0.38), while SO$_2^+$ / SO$^+$ showed the opposite trend (1.7–1.8 in CV vs. 1.0–1.5 in SV). This shift indicates that greater thermal decomposition occurs in the CV. The ratios of SO$_3^+$, HSO$_3^+$ and H$_2$SO$_4^+$ vs. SO$^+$ from H$_2$SO$_4$(g) in the NIST EI database are 2.0, 1.4 and 0.9 respectively (Linstrom and Mallard, 2016). Given that the ionization process is the same in the AMS and NIST, the much lower ratios of SO$_3^+$, HSO$_3^+$ and H$_2$SO$_4^+$ compared to SO$^+$ from (NH$_4$)$_2$SO$_4$ in the
SV (0.11–0.38) are indicative of substantial thermal decomposition occurring in the SV, which is even larger in the CV. In the NIST spectra database, standard 70 eV EI of SO$_2$(g) and H$_2$SO$_4$(g) yield SO$_2^+$ / SO$_3^+$ of $\sim$ 2 and $\sim$ 1 respectively (Linstrom and Mallard, 2016). Therefore, a possible explanation for the higher SO$_2^+$ / SO$_3^+$ in the CV is consistent with enhanced thermal decomposition in the CV, which produces more SO$_2$(g) than in the SV.

Although the exact ion ratios from each standard species are sensitive to the history and status (e.g. tuning or $T_e$) of a specific AMS, and can therefore vary among different AMSs, observations of larger fragments from NO$_3$ and SO$_4$ in the SV (compared to the CV) just described were consistent across all experiments over several years and also in other independent studies (Xu et al. 2017).

### Table 1. Fragmentation patterns of particulate nitrate from NH$_4$NO$_3$ particles and particulate sulfate from (NH$_4$)$_2$SO$_4$ 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 1 standard deviation.

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<th>Mass</th>
<th>Fragment</th>
<th>Relative intensity</th>
<th>Fraction (%)</th>
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<td>HR Mass</td>
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$^a$ All the isotope ions are calculated based on isotope ratios in fragmentation table, thus not shown here, and account for ~ 1 % of nitrate and ~ 3 % of sulfate in the SV and ~ 0.5 % of nitrate and ~ 3 % in sulfate in the CV. $^b$ From this study. $^c$ From Hogrefe et al. (2004).

3.1.2 Recommended adjustments to the fragmentation table for H$_2$O$^+$ and S$^+$ in the CV

Since the detection of nitrate and sulfate is different in the SV and CV, accurate quantification for the CV requires the use of an RIE$_{SO_4}$ determined with the CV. RIE$_{SO_4}$ ~ 1.2 was found in the SV in this study, the same as the default value in the AMS analysis software. RIE$_{SO_4}$ in the CV in this study was ~ 1.7–2.4, significantly larger than in the SV, although values as low as 1.1 have been observed in the CV with ACSM (Hu et al., 2017). Sulfate RIE can be influenced by many aspects including detailed ionizer, vapourizer, filament positions and turning of ion optics. Differences in the timescales on which sulfate particles fully vapourize on the SV and CV, as discussed in Sect. 3.2, could also give rise to differences in the measured RIE$_{SO_4}$ for different vapourizers.

The fragmentation tables used in the AMS software also need an adjustment for accurate mass quantification, as the contribution of ammonium sulfate to H$_2$O$^+$ and S$^+$ are dif-
different for the CV. The changes in the fragmentation table for the CV is shown in Table 2 based on the fragmentation pattern obtained in Table 1. These modifications need to be made for both the UMR and HR fragmentation tables. We note that the determination of sulfate and nitrate in mixed inorganic/organic aerosols (e.g., ambient air) includes subtraction of organic interferences at several m/z associated with inorganic ions (Allan et al., 2004b). It is expected that some fragmentation table entries that affect sulfate quantification (in particular frag_SO₃[48] and [64]) will need revision for an accurate quantification of mixed aerosols from UMR data. Higher coefficients for H₂O⁺ and S⁺ ions generated from SO₄ 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 SO₄ and thus do not affect the quantification of SO₄ if such a calibration is performed. These differences also suggest that fragmentation for the CV should continue to be investigated in future studies. We also note that the corrections can vary depending on the type of organics sampled, especially in laboratory and source studies, and thus individual users should always examine those corrections for specific experiments and modify them if needed.

### 3.1.3 Effect of Tᵥ

Tᵥ can substantially impact vapourization and thermal decomposition, and hence the fragmentation patterns as well as quantification in the AMS (Canagaratna et al., 2015; Docherty et al., 2015). The Tᵥ-dependent fragmentation patterns can help to understand the detection process for both vapourizers, and also help to determine the optimum Tᵥ for the CV. In this study, fragmentation patterns of four inorganic standards (NH₄NO₃, NaNO₃, (NH₄)₂SO₄, and NH₄Cl) over the entire usable range of Tᵥ (200–800°C) in both the SV and CV are explored (Fig. 4).

**NH₄NO₃**

In the SV, NO⁺² / NO⁺ from NH₄NO₃ decreased by ~ 40 % while Tᵥ increased from 200 to 750°C (Fig. 4a). A possible explanation for this decreasing trend is that higher Tᵥ increases the fraction of the nitrate that thermally decomposes into smaller molecules. For the CV, NO⁺² / NO⁺ varied within a small range, and was an order of magnitude...
lower (0.015–0.04) than for the SV, as discussed above. NO$_2^+$/NO$^+$ in the CV at $T_v = 200^\circ$C (0.04) was much lower than in SV at $T_v = 750^\circ$C (0.5), suggesting the thermal decomposition was stronger in the CV even at low $T_v$ due to the increased vapour collisions and residence time.

NaNO$_3$

NaNO$_3$ is less volatile than NH$_4$NO$_3$ with melting and boiling points of 306 and 380°C respectively, substantially higher than for NH$_4$NO$_3$ (melting point of 169° and boiling point of ~210°; Haynes, 2015). Since boiling points are referenced to 1 atm, these species will boil at lower temperatures under the vacuum of the AMS vapourizer. Here we are using the boiling points as indicators of relative volatility of different species. In the SV, NO$_2^+$/NO$^+$ ratio for NaNO$_3$ ranged from 0.1 at 200°C and 0.005 at 550°C, which is 10–100 times lower than typical values from NH$_4$NO$_3$ (0.29–0.75) (Fig. 4b). Much lower NO$_2^+$/NO$^+$ from NaNO$_3$ compared to NH$_4$NO$_3$ at $T_v = 600^\circ$C have also been reported in prior studies with SV in AMS (Bruns et al., 2010). A greater thermal decomposition due to a longer residence time of the particles on the vapourizer surface (resulting from slower vapourization) for NaNO$_3$ than NH$_4$NO$_3$ and different thermal decomposition pathways (as NaNO$_3$ cannot produce HNO$_3$(g)) are two possible explanations. In the CV, much lower NO$_2^+$/NO$^+$ ratios for NaNO$_3$ (0.001–0.006) were observed compared to those from the SV (0.005–0.1), consistent with the results for NH$_4$NO$_3$.

(NH$_4$)$_2$SO$_4$

Some $T_v$-dependent changes of SO$_2^+$/SO$^+$ ratios were observed for both vapourizers (Fig. 4c). As $T_v$ increased, the relative abundance of the heavier ions (HSO$_3^+$ and SO$_3^+$) decreased and SO$_2^+$ increased, consistent with increasing thermal decomposition of (NH$_4$)$_2$SO$_4$ with more abundant SO$_2$(g) and lower H$_2$SO$_4$(g) in the thermal decomposition products. In contrast to the continuous variation of SO$_2^+$/SO$^+$ ratios in the SV over the entire $T_v$ range, the CV only showed a change of SO$_2^+$/SO$^+$ below $T_v = 300^\circ$C and then levelled off. This indicates that the thermal decomposition process of already vapourized sulfate (within several-second timescale of MS mode) is complete in the CV at $T_v > 300^\circ$C.

NH$_4$Cl

The thermal decomposition of NH$_4$Cl particles is expected to occur through the reaction (Zhu et al., 2007) NH$_4$Cl(s) $\rightarrow$ NH$_3$(g) + HCl(g). The main fragments from chloride in the AMS are HCl$^+$ and Cl$^+$ (Allan et al.,...
2004b). In this study, Cl$^+/HCl^+$ vs. $T_v$ from both vapourizers are within a narrow range (0.17–0.27), which is similar to the 70 eV EI fragmentation pattern of HCl(g) in the NIST database (Cl$^+/HCl^+$ = 0.17; Linstrom and Mal- lard, 2016) and also consistent with the Cl$^+/HCl^+$ ratio observed in other ambient data sets (0.175–0.24) (Hu et al., 2016). Compared to much larger changes for NO$_3$ and SO$_4$ fragment ion ratios, the differences in HCl$^+/Cl^+$ ratio between the vapourizers and temperatures are relatively small. This suggests, for Cl$^+$ and HCl$^+$, that the thermal decomposition and ionization fragmentation of NH$_4$Cl particles are similar for both vapourizers across different temperatures, and likely mainly produced from direct ionization of HCl(g). We note that unlike NO$_3$ or SO$_4$, HCl(g) does not have a thermal decomposition pathway.

The small variations of Cl$^+/HCl^+$ vs. $T_v$ may have been due to the changing background of Cl$^+$ and HCl$^+$ due to the different stickiness of chloride decomposition products on the vapourizer surface and ionization chamber walls. Drewnick et al. (2015) reported that Cl$^+$ had a slowly evolving background signal (8 to > 30 min at $T_v$ ∼ 600–720°C). We evaluated this effect by examining Cl$^+$/HCl$^+$ at the same $T_v$ (∼ 600°C) after increasing $T_v$ from ∼ 600 to 850°C, and then returning to 600°C. We found that Cl$^+$/HCl$^+$ decreased by 25% in the SV and by 5% in the CV compared to the values before $T_v$ was changed (Fig. 4d). This hysteresis behaviour supports the assumption that changes in the slowly evaporating signals were likely the main reason for the observed variations of Cl$^+$/HCl$^+$ ratios at different $T_v$.

Drewnick et al. (2015) suggested that tungsten oxide chloride (WO$_2$Cl$_2$(g)) is detected in AMS spectra from the interaction between sampled chloride aerosol species and vapourizer surfaces, although signal levels are very small, e.g. 0.04% of the total NH$_4$Cl signal. In this study, some ions that were consistent with WO$_2$Cl$_2$ species, namely WCl$^+$ and WO$_2^+$, were also observed when sampling NH$_4$Cl with SV. The abundance of those ions was very low (< 0.02%), similar to observations by Drewnick et al. (2015). Jimenez et al. (2003) reported MoO$_2^+$ and MoO$_2^+$ when sampling iodine-oxides with a prototype AMS vapourizer made of molybd-enum. Following that work, we searched for the MoO$^+$, MoO$_2^+$ and MoCl$^+$ signals in the CV, but saw no detectable enhancement of either ion when sampling NH$_4$Cl and other inorganic species in this study.

**NH$_4$ ions from NH$_4$ NO$_3$, (NH$_4$)$_2$SO$_4$ and NH$_4$Cl**

The abundance of NH$_4^+$ ions (NH$_4^+ = NH^++NH_2^++NH_3^+$) from three NH$_4$-containing species (NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$ and NH$_4$Cl) vs. $T_v$ is shown in Fig. 4e–f. The fragmentation patterns of NH$_4$ across the different vapourizers and compounds were very similar. The fragmentation pattern of NH$_4$ in AMS was very consistent with the standard patterns of NH$_3$(g) for 70 eV EI in the NIST database (Fig. 4e–f; Lin- strom and Mallard, 2016). A stable fragmentation pattern of NH$_4$ as a function of $T_v$ (with variations of those abundances smaller than 4%) also suggests that thermal decomposition played a very minor role after NH$_3$(g) vaporization.

### 3.1.4 Effect of particle beam position on the vapourizer

A key component of the AMS is an aerodynamic lens that focuses particles into a very narrow beam that is focused onto the centre of the vapourizer (Liu et al., 1995a, b; Jayne et al., 2000). The alignment of the particle beam with the vapourizer centre (typically referred to as a “lens alignment”) is checked regularly, as a misalignment can lead to particle losses and underestimation of particle concentrations. Lens alignment is usually performed with 300 nm pure NH$_4$NO$_3$ particles, since these particles are known to be easily focused (∼ 0.5 mm beam diameter at the vapourizer) and a CPC is used to verify stable particle concentration during sampling (typically within 5% during an experiment). The lens position is varied (first horizontally and later vertically, or vice versa), and the edges of vapourizer can be identified by a steep variation in aerosol signal. A microcalliper is used to read the lens position during this experiment. In a CV AMS, lens alignment requires greater precision, since the entrance of the vapourizer is narrower than for SV (Fig. 1a). Lens alignment effects on signal intensity, fragmentation patterns, and size distributions of NH$_4$NO$_3$ for both vapourizers are discussed below. Since the cross section of the vapourizer is radially symmetrical, lens alignment results from horizontal and vertical movements are generally very similar. Hence, only data from the horizontal dimension are shown (Figs. 5–6).

For these experiments, the lens was first aligned such that the particle beam almost missed the vapourizer on the left side and a low NO$_3^-$ signal was observed. Then the particle beam was moved stepwise toward the edge of the vapourizer, which was identified by the sharp increase of NO$_3^-$ signal, then to the centre of vapourizer and finally to the other edge. For both vapourizers, the NO$_3^-$ signal shows a symmetrical variation with a broad plateau in the centre (Figs. 5–6). In the CV, low NO$_3^-$ / NO$^+$ (∼ 0.07) is observed in the vapourizer centre as previously discussed (Fig. 3a). However, a much higher NO$_3^-$ / NO$^+$ ratio (0.6–0.8) was observed at the edges of the vapourizer (Fig. 5). These values are similar to those observed for the centre of the SV (0.2–0.7). The higher NO$_3^-$ / NO$^+$ ratios on the edges of the CV are consistent with the results of Xu et al. (2017). This is likely caused by the lack of wall collisions for vapour molecules inside of the CV when the particle beam hits the CV edge. The edge position is illustrated in Fig. 1a. This enhanced NO$_3^-$ ion signal on the edge of the vapourizer can also be used to determine the centre of the lens alignment. When the beam is off the outside edge of the vapourizer assembly, a small signal can still be observed since the particles impact on another surface.
In the CV, the total nitrate signal also showed two peaks at the edge positions, 10–20% higher than at the centre. The slightly higher NO$_3^-$ signal at the edge of the CV may be due to (1) a higher IE$_{NO_3}$ resulting from the different spatial distribution of vapour molecules, which may better overlap the electron beam and/or ion extraction regions; (2) a higher IE$_{NO_3}$ due to longer residence time of the molecules in the electron beam due to the lower vapour molecule velocity resulting from the lower temperature at the front end of the CV or (3) a different RIE of the particle vapour resulting from a change in thermal decomposition products on the vapourizer. For example, at the edge the HNO$_3$(g) fraction may be higher than at the centre. HNO$_3$(g) has a higher cross section than NO$_2$(g) and NO(g) due to its higher molar weight (and possibly a lower velocity). Thus it may result in more ions being formed. The higher NO$_3^-$ signal on the left edge than on the right edge may be due to the right side being closer to the heated filament that supplies electrons for the ionization process, thus resulting in slightly larger overlap with the electron cloud and increasing ionization efficiency. Supporting this hypothesis, equal enhancement of NO$_3^-$ signal on the edges was observed for lens alignment in the vertical direction (not shown). In the SV, we did not observe this enhanced nitrate signal on the vapourizer edge (Fig. 6), which is consistent with the smaller difference in NO$_2^+$/NO$_3^+$ between the vapourizer centre and edge, and the fact that hitting the centre as opposed to the edge of the SV is not expected to greatly change the number of vapour–wall collisions. The reason for the slightly increasing trend of NO$_2^+$/NO$_3^+$ ratios toward the filament side in Fig. 6 is unclear.

In contrast to the variable NO$_2^+$/NO$_3^+$, NH$_3^+$/NH$_3^+$ and NH$_3^+$/NH$_4^+$ from NH$_4$ did not show systematic differences between the centre and the edge of both vapourizers. The constant ratios support direct EI ionization on NH$_3$(g) as discussed above. Slightly lower RIE$_{NH_4}$ are observed at the edges of the CV, which might be due to changes in the mixture of vapour species formed from nitrate (HNO$_3$(g), NO$_2$(g) and NO(g)), while the vapour formed from NH$_4$ stays the same (NH$_3$(g)). In the SV, we did not find systematic differences of RIE$_{NH_4}$ between the centre and edges, within their higher uncertainties (Fig. 6).
Figure 6. SV: particle beam position dependence of NO$_2^+$ / NO$^+$, total nitrate, NO$_3^+$ and NO$^+$ signals, RIE$_{NH_4}$, NH$_3^+$ / NH$^+$, NH$_2^+$ / NH$^+$ and nitrate equivalent mass ratio of CO$_2^+$/NO$_3^-$. The shaded areas are a rough indication of where the particle beam hits the vapourizer. A constant IE obtained with pure NH$_4$NO$_3$ particles at the centre of the lens was applied to all data collected in this experiment. The error bars represent the measurement variability (standard deviation) for 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 centre 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 in the rest of this paper.

The size-resolved detection of NO$_2^+$, NO$^+$, NH$_3^+$ and NH$_2^+$ at the edge and centre of both vapourizers is shown in Fig. 7, and was achieved by using PToF acquisition mode in the AMS. The PToFs are the sum of particle travel time and time vapourization and detection. In these experiments particles of 300 nm NH$_4$NO$_3$ were size selected using a DMA. When directing the particle beam onto the edge of the CV, all ions peaked at the same time (Fig. 7a), but when the beam was directed towards the centre the rise time of different ions was in the order NO$_2^+$ < NH$_2^+$ / NH$^+$ < NO$^+$ (Fig. 7b). The different rise time likely reflects the increasing residence time of each precursor vapour in the CV cavity, presumably due to increasingly strong interactions with the surface. The same qualitative trend can in fact be observed for tails in the SV in Figs. 7c and 12a. The peak time when the particle beam hits the centre of the CV is 200 µs or more later than when hitting the CV edge. This delay represents a rough desorption and escape time for vapours from the CV cavity. In the SV, consistent peak times were observed at all vapourizer target positions, indicating that the delayed peak time at the centre of the CV is due to trapping in the cavity. The measured PToF time distributions when impacting the edge of the CV are as narrow as those from the SV. Thus, changing the lens alignment to focus particles on the CV edge can be used to obtain higher-resolution size distributions in the CV for more volatile species, although presumably with degraded quantification of the total concentration.

3.1.5 Production of CO$_2^+$ from inorganic species

Pieber et al. (2016) have recently shown that CO$_2^+$ can be produced on the surface of the SV while sampling inorganic particles, presumably from the oxidation/decomposition and release of vapours from residual carbonaceous material on the vapourizer. This causes an interference in the quantification of organic species, which needs to be corrected by adjustments to the fragmentation table using experimental results for an individual AMS instrument (e.g. the measured CO$_2^+$/NO$_3^-$ ratio during IE calibrations with NH$_4$NO$_3$). The reported mass ratio (nitrate equivalent mass, i.e. using RIE = 1) of the CO$_2^+$ produced vs. the inorganic an-
Figure 7. Size-resolved detection of NH$_4$NO$_3$ (DMA selected 300 nm particles, including some larger doubly charged particles) major ions using the PToF acquisition mode at (a) the CV edge (position = 7.6 mm in Fig. 5), (b) the CV centre (position = 7.1 mm in Fig. 5), (c) SV edge (position = 8.4 mm in Fig. 6) and SV centre (position = 7.9 mm in Fig. 6). All the peaks were normalized to the NO$^+$ maximum. Note that the size distributions of the particles were identical within each panel, and that the differences observed between the different ions are due to vapourization and other effects. (see main text). The experiments for the SV and CV were performed at different times, and the fraction of doubly charged particles was lower for the SV experiment.

The CO$_2^+$ signal observed when sampling NH$_4$NO$_3$ in both vapourizers is shown in Fig. 8a. The data were obtained after 4 days of exposing both AMSs ($T_v = 500–600$ °C) to 10–1000 µg m$^{-3}$ of SOA generated during the chamber experiments, which could enhance this interference. Similarly to Pieber et al. (2016), a CO$_2^+$ / nitrate mass ratio (RIE = 1 were applied to both) of 1.5% was observed for the SV (0.7% before exposure). In contrast, negligible CO$_2^+$ was observed for the CV. We further investigated this effect as a function of $T_v$ (200–800°C; Fig. 8b). Negligible CO$_2^+$ (CO$_2^+$ / nitrate < 0.4%) was observed for the CV over the entire $T_v$ range, whereas in the SV, ratios of ~1.2% were observed below 450°C and increased ratios up to 3% were observed at 700–750°C. The negligible CO$_2^+$ formation from NH$_4$NO$_3$ in the CV may be due to the difference in thermal decomposition pathways between the CV and SV. As discussed above, the main product of nitrate in the CV is likely NO(g), which is not an efficient oxidizer compared to NO$_2$(g). The difference in the vapourizer materials might also play a critical role, as molybdenum is more inert than tungsten (Xu et al., 2017) and may highlight the different catalytic properties of the metals. CO$_2^+$ / NO$_3^-$ ratios that are dependent on lens alignment are shown in Figs. 5–6. No dependence of CO$_2^+$ / NO$_3^-$ ratios in the SV with lens alignment was found (Fig. 6). However, in the CV, the CO$_2^+$ / NO$_3^-$ ratios are a little higher at the vapourizer edge (Fig. 5), which is consistent with high NO$_2^+$ / NO$^+$ ratio there.

However, when sampling NaNO$_3$ particles, CO$_2^+$ formation was observed in the CV (Fig. 8b). Two experiments were conducted, one with a “cleaner” CV (sampling little to no organic aerosols for days) and the other (“dirty”) was done the day after exposing the CV to 10–1000 µg m$^{-3}$ of SOA from chamber studies for four days (dirty CV). For the cleaner CV, CO$_2^+$ / nitrate for NaNO$_3$ (0.3–1.2%) was lower than for SV (1.2–12%), especially below 400°C. For the dirty condition, high ratios were observed above 500°C for the CV (4–11%) and above 700°C for the SV (4–9%). The fundamental reason for CO$_2^+$ artefact in the CV from NaNO$_3$ (but not NH$_4$NO$_3$) is not clear. Higher CO$_2^+$ / NO$_3^-$ ratios when sampling NaNO$_3$ particles in the SV than with NH$_4$NO$_3$ par-
particles have also been observed in this (Fig. 8b) and previous studies (Pieber et al., 2016).

3.2 CE of standard inorganic species

The CE of laboratory aerosol containing four inorganic species (NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, NaNO$_3$ and NH$_4$Cl) in the CV is investigated here. The ratio of the mass concentrations of monodisperse particles as calculated for the AMS (using CE = 1) and CPC-derived concentrations (hereafter referred to as “AMS / CPC mass ratio”) are shown in Fig. 9 as a function of $T_v$. To our knowledge, this is the first time that AMS CE has been reported as a function of $T_v$ for SV. All the AMS / CPC mass ratios (interpreted as CE) were calculated based on the IE and RIE obtained at 550–600 °C. Field results suggest that RIE is not a strong function of temperature in the 350–600 °C range (Jimenez et al., 2016).

Particle sizes of 250–300 nm were used to avoid particle losses by any other mechanism than bounce at the vapourizer (Huffman et al., 2005; Liu et al., 2007; Bahreini et al., 2011). Thus a correction factor is required for correction of the NaNO$_3$ data for lens transmission losses, so that the corrected ratio can be interpreted as CE due to vapourizer bounce only. Based on the measured lens transmission curves for the instruments used in this study (Fig. S2), lens transmission fractions $E_L = 0.6$ and 0.8 were applied to the AMS / CPC mass ratio of 300 nm NaNO$_3$ in the SV and CV respectively. No lens transmission corrections are needed for the other species.

3.2.1 NH$_4$NO$_3$

The AMS / CPC nitrate mass ratio vs. $T_v$ is shown in Fig. 9a1. An average ratio of 1.03 ± 0.07 (avg. ± stdv; range: 0.89–1.12) for $T_v = 200$–750 °C was observed for the SV. The variation of AMS / CPC mass ratios at other $T_v$ compared to 600 °C (~12 %) was consistent with the reported 10 % variation in the AMS response to ambient particles as $T_v$ was rapidly varied (Docherty et al., 2015). The ratio of background signal (closed particle beam) to aerosol input (CPC mass) was small, and exhibited a continuous decrease (0.12 to 0.04) with $T_v$, presumably due to somewhat slower vapourization at lower $T_v$.

In the CV, the AMS / CPC mass ratio of NH$_4$NO$_3$ was approximately 1 between 300 and 700 °C, with lower ratios (~0.6–0.8) at extreme $T_v$ ($T_v < 300$ °C or $T_v > 700$ °C). The decreased AMS / CPC mass ratio at low $T_v$ may be ascribed to slower vapourization. Similarly to the SV, this was supported by a larger closed signal at lower $T_v$, e.g. ~0.12 at 200 °C vs. ~0.005 at 500 °C. Possible reasons for the decrease at the highest $T_v$ (>700 °C) are stronger interactions of the analytes with the hot vapourizer surfaces, which is supported by a slightly higher nitrate closed signal observed at high $T_v$, and/or a faster molecular speed reducing the effective ionization efficiency. To further examine this question, we study the aerosol signal decay and rise upon blocking and unblocking the particle beam (Fig. 10).
During typical MS mode operation, the beam-open and beam-blocked (closed) positions are alternated every several seconds (usually ~ 5 s). During the particle beam modulation experiments, these intervals were extended to much larger values, typically 5–10 min, to allow for studying the signal response at much longer times, similarly to the study performed by Drewnick et al. (2015). The time resolution used was 1–3 s. Three $T_v$ spanning the usable range (200, 600 and 850 °C) were selected to perform the experiments in both vapourizers, as shown in Fig. 10. For the medium $T_v = 600$ °C, a rapid increase and decrease in the nitrate signal ($\tau < 1$ s) was observed in both vapourizers. $\tau$ 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 vapourizer is not shown, since it varies in the same way. Note that the $\tau$ might change over time for sticky or semi-refractory species (e.g. NaCl or FeCl$_3$) (Drewnick et al., 2015).

After blocking the particle beam, the nitrate signal decreased to 8% of the beam-open signal after 3 s in the SV and to 1% after 1 s in the CV. Thus faster nitrate decay in the CV than the SV has been observed. We speculate that the scattered particles onto a nearby surface of the ionization chamber could result in a slower decay due to the colder chamber surfaces. As the CV inhibits particle bouncing/scattering, this results in a faster decay. This clearer separation of processes is one of the advantages of the CV over SV. At lower $T_v = 200$ °C, the nitrate signal decays to 16% of the 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. A slower rise of the nitrate signal at $T_v = 200$ °C was also observed in the CV upon unblocking the particle beam, which resulted in a lower open signal detection in the conventional MS mode (where the beam would be blocked again after a few seconds). Thus this experiment...
Figure 10. Results of an experiment slowly alternating beam-open and beam-closed positions while sampling NH$_4$NO$_3$ and 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 vapourizer 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.

indicates that the longer time for the vapours produced from nitrate to escape the CV (and possibly for vapourization) at lower $T_v$ was the reason for the lower nitrate signal detected in this case. At the higher $T_v$ of 850 °C, a faster decay of the nitrate signal (3 % of open signal in 3 s) than at 600 °C (8 %) was observed in the SV. In the CV, the beam-blocked signal remained elevated (∼20 % of open signal) and constant for the rest of beam-blocked time (∼5 min). This elevated background signal at higher $T_v$ (> 700 °C) may be due to either (1) the hotter surroundings of the ionizer cage containing deposited nitrate resulting in more desorption of nitrated vapours; and/or (2) stronger interactions between the species decomposing from nitrate and the hot vapourizer surfaces.

3.2.2 NaNO$_3$

AMS / CPC mass ratios for NaNO$_3$ are shown in Fig. 9b. As $T_v$ increases from 200 to 700 °C, AMS / CPC mass ratios of NaNO$_3$ in SV increased dramatically (from 0.02 to ∼0.85), indicating a greatly improved detection of NaNO$_3$ at higher $T_v$ (> 500 °C). When $T_v$ was above 550 °C, the nitrate $\tau$ was less than 2 s (beam blocked = 7 % of beam open at $T_v$ = 600 °C), indicating that vapourization was fast enough for nitrate detection from NaNO$_3$ in MS mode. The ratio of ∼0.85 is indicative of a minor or particle bounce for NaNO$_3$.

In the CV, AMS / CPC mass ratios of NaNO$_3$ showed a qualitatively similar positive trend with $T_v$. However, the ratio in the CV peaked at a much lower $T_v$ (300 °C) than for SV (500 °C), indicating better detection of less-volatile species in the CV, presumably due to the increased residence time and reduced bounce (or higher probability of finally vapourizing after multiple collisions inside the CV). For the beam-open and beam-blocked experiment (Fig. 10), much faster particle decay was observed in the CV ($\tau$ ∼ 1 s at 310 °C) than in the SV ($\tau$ ∼ 12 s at 330 °C) at these temperatures. This difference may be due to the geometry of the CV, which inhibits the particle bounce from the vapourizer to the surrounding colder ionizer surfaces, and this effect can lead to a slowly evolving signal in the SV. Above 550 °C, the ratio in both vapourizers levelled off at 0.8–0.95. The partial cause of
the plateau of the AMS / CPC mass ratio for NaNO$_3$ at less than 1 in the CV is probably due to the uncertainty of particle lens transmission loss correction. A full capture of NaNO$_3$ ($E_b = 1$) in the capture vapourizer was reported based on the AMS internal light scattering data (counting individual particles) (Xu et al., 2017). Another possible reason for lower NO$_3$ detection efficiency is that a Jayne shape factor (similar to NH$_4$NO$_3$) might be needed to correct the NaNO$_3$ density (2.26 g cm$^{-3}$). The RIE of nitrate from NaNO$_3$ might also be slightly lower than from NH$_4$NO$_3$ due to their different vapour precursors. Compared to the theoretical ion balance (mole ratio = 1), mole ratios between detected Na and NO$_3$ in both vapourizers were very low (< 0.04) based on an assumed RIE of Na of 1. Na is a semi-refractory species (probably exists as Na$_2$O after thermal decomposition) that cannot be fully vaporized on the vapourizer, and it might retain some of the nitrate in the vapourizer for a longer period.

3.2.3 (NH$_4$)$_2$SO$_4$

Pure (NH$_4$)$_2$SO$_4$ is a less-volatile species and has been reported to have an $E_b$ of 0.2–0.4 (200 nm) in the SV at $T_v = 600$°C when sampling at ambient RH below its deliquescence point (Allan et al., 2004a; Matthew et al., 2008), while dry mixed ammonium sulfate-organic ambient particles typically have $E_b \sim 0.5$ (Middlebrook et al., 2012). In this study, a positive dependence of the AMS / CPC SO$_4$ mass ratio vs. $T_v$ was observed for the SV, increasing from 0.2 at $T_v = 200$°C to 0.55 at $T_v > 500$°C (Fig. 9c1). This increase is likely due to both a lower particle bounce fraction and also faster vaporisation. The $\tau$ of SO$_4$ after blocking the particle beam was 26 s at $T_v = 310$°C and < 2.5 s at $T_v = 850$°C (Fig. 11).

In the CV, AMS / CPC mass ratios of SO$_4$ were reproducibly 0.7–0.8 at $T_v = 400$–700°C based on multiple experiments (Fig. 11). The AMS / CPC mass ratios of dry (NH$_4$)$_2$SO$_4$ in the CV that are less than 1 are consistent with the results of Xu et al. (2017). The ∼ 25 % missing signal suggests that a small fraction of pure (NH$_4$)$_2$SO$_4$ particles might still bounce on the edge of the CV (interpreted as $E_b$) or that they may still bounce out of the CV without vaporizing inside the CV cavity. $E_b$ probably contribute at least a few percent to (NH$_4$)$_2$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 labelled in Fig. 1). However, compared to the ratios of ∼ 0.45–0.55 in SV, pure (NH$_4$)$_2$SO$_4$ is more efficiently detected in the CV. The beam-open and beam-blocked comparison also showed a much faster decay of SO$_4$ in the CV than in the SV for similar $T_v$, e.g. $\tau < 2$ s in the CV vs. $\tau = 13$ s in the SV at $T_v = 550$–610°C. As discussed above, the faster decay of signals in the CV is likely due to the lower fraction of particle bouncing to the surrounding ionizer cage than with the SV. The reduced AMS / CPC mass ratios at lower $T_v$ in both vapourizers were probably caused by slower vapourization of sulfate (slow rise and decay signal in Fig. 11) and/or enhanced particle bounce at low $T_v$. The reason for the lower AMS / CPC mass ratio at higher $T_v$ (> 700°C) in the CV may be due to enhanced interactions with the hot vapourizer surfaces, as hypothesized above for nitrate. Enhanced beam-blocked signal was observed at high $T_v$ (Fig. 9c2), as observed for NH$_4$NO$_3$ and NaNO$_3$.

3.2.4 NH$_4$Cl

As discussed above, chloride appears to be very sticky on the vapourizer/ionizer surface, and is only slowly removed from the AMS background (Drewnick et al., 2015). Thus, the instrument history (e.g. chloride sampled and/or recent $T_v$ history) or set up (e.g. different duty cycles) may influence NH$_4$Cl detection.

Huffman et al. (2009b) reported that NH$_4$Cl particles were vaporised in a thermodenuder at a higher temperature than NH$_4$NO$_3$ but a lower temperature than (NH$_4$)$_2$SO$_4$. However, the melting point/ decomposition point of pure NH$_4$Cl is ∼ 330°C (Zhu et al., 2007), which is higher than those of (NH$_4$)$_2$SO$_4$ (235–280°C) (Haynes, 2015). AMS / CPC mass ratios of Cl from NH$_4$Cl (300 nm) in the SV were reproducibly 0.2–0.25, possibly due to particle bounce and slow vaporization of bounced particle from the ionizer cage surfaces. High background signals and a slow timescale of change were observed at all $T_v$ for the SV (Figs. 9 and 11), consistent with the importance of the second hypothesis.

Slightly larger AMS / CPC mass ratios (0.27–0.35) were observed for the CV at $T_v > 400$°C. Two separate AMSs showed similar AM / CPC ratios (0.33–0.37) at $T_v = 550$–600°C. The beam-open and beam-blocked experiment showed a faster chloride decay in the CV (τ = 5.2 s) than the SV (τ = 104 s) at 550–600°C, mainly determined by the slower decaying Cl$^+$ ion (while the HCl$^+$ ion response was faster).

3.2.5 NH$_4$ from NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$ and NH$_4$Cl

For both the SV and CV, the AMS / CPC mass ratios of NH$_4$ showed similar values and $T_v$ dependences to their anions (Fig. 9). This is an indication that particle bounce played an important role for AMS / CPC mass ratios less than 1.

At medium $T_v$ (500–650°C), NH$_4$ from the three species in both vapourizers all showed very low background signals (< 0.5 %). In the beam-open and beam-blocked experiment, the decay lifetime of NH$_4$ was below 1–2 s, which was similar to or faster than the anion decays. The faster vaporization of NH$_4$ than for the anion has also been reported before for vaporization of ambient aerosols in a thermodenuder, where aerosols became more acidic when being heated (Huffman et al., 2009a). Despite the lower background signals of NH$_4$, low AMS / CPC mass ratios of NH$_4$ from (NH$_4$)$_2$SO$_4$ and NH$_4$Cl in both vapourizers was observed, strongly suggesting particle bouncing as the most likely explanation for the
lower ratios of (NH$_4$)$_2$SO$_4$ and NH$_4$Cl observed in the CV as well.

At lower $T_v$ (< 350°C), NH$_4$ from the three inorganic species in the SV showed similar decay lifetimes (< 2 s) to the one at medium $T_v$ (500–650°C) and was much faster than their anion decays (2–184 s). NH$_4$ decay in the CV at low $T_v$ (∼ 200–330°C) exhibited a $\tau$ ∼ 16 s for NH$_4$NO$_3$, ∼ 2 s for (NH$_4$)$_2$SO$_4$ and 10 s for NH$_4$Cl, which was longer than NH$_4$ in the SV at a similarly low $T_v$ range. The longer NH$_4$ decay suggested a slower release of NH$_3$($g$) for the CV than the SV at this low $T_v$ range (∼ 350°C), the reasons for which are unclear. The NH$_4$ decay in the CV was still faster than their anions of SO$_4$ and Cl, which may explain why AMS / CPC mass ratios of NH$_4$ were higher than SO$_4$, and Cl and anion/cation ratios (0.2 to 1) decreased at lower $T_v$ (400°C; Fig. 9b2–3 and d2–3). At higher $T_v$, AMS / CPC mass ratios of NH$_4$ exhibited similar ratios to their anions. A small background enhancement at higher $T_v$ in the CV was also observed.

3.2.6 Implications for vapourization mechanisms in the AMS

It has recently been suggested that a major fraction of NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ vapourize as intact salts in the AMS (Murphy, 2016, 2017). Separate vapourization to NH$_3$($g$) and H$_x$NO$_y$($g$) followed by their separate ionization can explain the high similarity of the ammonium fragmentation pattern to that of NH$_3$($g$) in the NIST EI database (Linstrom and Mallard, 2016) (Fig. 4). It can also explain constancy in the fragmentation pattern of ammonium across vapourizers and $T_v$ (Fig. 4), despite major simultaneous changes on the observed fragmentation patterns of sulfate and nitrate. These very different fragmentation behaviours and trends between the cation and anion would be unexpected if inorganic species vapourized as intact salts. If molecular salts were vapourized, species such as NH$_4$NO$_3^+$, (NH$_4$)$_2$SO$_4^+$, and NH$_4$Cl$^+$ would form after ionization. Since the fragmentation chemistry of molecular cations is highly dependent on the species (e.g. McLafferty and Turecek,
were quickly vapourized and detected after impact on the open SV surface. The rise time is defined as the time interval from 10% of peak height to the peak. 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 NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ in the CV from Xu et al. (2017). Although it will lead to lower sizing resolution, it clearly shows that size distributions can still be measured with the CV. 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 times between the CV and SV are different for different species (e.g. 0.5 ms for NO$_3$ and 1.3 ms for SO$_4$), which suggests that the CV could benefit from different size calibration curves for externally mixed aerosols. The earlier rise of NO$_3^-$ than NO$_2^+$ in inorganic nitrates in the CV may be due to reduced surface interactions of HNO$_3$ (g) and NO$_2$ (g) (which can yield NO$_2^+$ ions) than for NO(g). In contrast to inorganic nitrates, NO$_2^+$ from organic nitrates showed a delayed tail vs. NO$_2^+$. This tail has also been seen in the CV for other organic nitrates from NO$_3$ radical + monoterpene chamber studies, and might be a useful approach to identify and quantify organic nitrates (e.g. Fry et al., 2013) when using the CV.

NH$_4$ from inorganic species in the CV showed a slightly earlier rise than NO$_3^+$ and SO$_4^{2-}$/SO$_4^{2+}$ (Fig. 12e and g). This may be associated with faster vapourization of NH$_3$ (g) and faster effusion out of the CV due to its lower molecular weight and reduced surface interactions.

### 3.3.2 Distribution as a function of temperature

PToF distributions of monodisperse particles from three standard species (250 nm (NH$_4$)$_2$SO$_4$, 300 nm NH$_4$NO$_3$ and 300 nm NaNO$_3$) in both vapoourizers as a function of $T_v$ are shown in Fig. 13a1–c1 and a2–c2. Figure 13a–c3 is a summary of FWHM as a function of $T_v$ based on Fig. 13a1–c1 and a2–c2. In the following discussion, three different aspects including transition $T_v$, peak broadening, and PToF vs. MS mode are discussed. The PToF distribution of each species reported is the sum for all its ions, and thus is a convolution of slightly different behaviours from each ion, as shown for example in Fig. 12.

**Transition $T'_v$ ($T_{v,t}$)**

$T_{v,t}$ is defined as the $T_v$ above which the measured particle distribution is no longer broadened by slow vapourization effects (<1 ms for nitrate and sulfate in the SV, 2 ms for sulfate in the CV). Above this $T_v$, stable peak shapes and similar peak widths are typically observed (Fig. 13a3–c3). $T_{v,t}$ appears to be mainly a function of species volatility with values for NH$_4$NO$_3$ (∼280°C) < (NH$_4$)$_2$SO$_4$ (∼380°C) < NaNO$_3$ (∼630°C) in the SV. This sequence is similar to the order of reported melting point trends.
for those species: \( \text{NH}_4\text{NO}_3: 169^\circ C < (\text{NH}_4)_2\text{SO}_4: 235–280^\circ C < \text{NaNO}_3: 306^\circ C \) (Haynes, 2015), as well as their boiling points, as shown in Fig. 14. Similar positive trends were also observed in the CV, where \( T_{\nu, t} \) of \( \text{NH}_4\text{NO}_3 \) and \( (\text{NH}_4)_2\text{SO}_4 \) in the CV were similar for \( \text{NO}_3^–(\sim 200^\circ C) \) and \( \text{SO}_4^{2–}(370^\circ C) \) with the SV, and \( T_{\nu, t} \) of \( \text{NaNO}_3 \) is slightly lower than the SV (630\(^\circ C\)). The lower \( T_{\nu, t} \) of \( \text{NaNO}_3 \) was probably due to less particle bounce and thus less delayed particle signals (Robinson et al., 2017) in the CV than SV. \( \text{NH}_4 \) from \( \text{NH}_4\text{NO}_3 \) in the CV show a higher \( T_{\nu, t}(380^\circ C) \) than in the SV (280\(^\circ C\)). A slower vapourization of \( \text{NH}_4 \) than \( \text{NO}_3 \) for the CV at low \( T_{\nu} \) was also observed in the beam-open and beam-blocked experiment (Fig. 10).

The relationship between \( T_{\nu, t} \) and melting/boiling points could probably be used for estimating whether pure species are detected in AMS sizing mode. For example, the anion of \( \text{NaNO}_3 \) or species with lower than or similar melting points to \( \text{NaNO}_3 \), e.g. \( \text{MgNO}_3 (129^\circ C) \) or \( \text{KNO}_3 (334^\circ C) \), can likely be detected and quantified by the CV at 600\(^\circ C\) in both MS and PToF modes. Further research on less-volatile species detection in the CV AMS, as well as the correlation of their fast detection \( T_{\nu} \) with melting and boiling points, is recommended.

The peak widths of \( \text{NH}_4\text{NO}_3 \) (both \( \text{NH}_4 \) and \( \text{NO}_3 \)) at higher \( T_{\nu} (>700^\circ C) \) start to broaden in the CV. The explicit reason for this broadening is unknown.

**Peak broadening in CV**

For monodisperse particles, the peak width of the AMS PToF distribution is primarily governed by thermal vapourization and decomposition rates and rate of effusion of particle vapours to exit the CV (Drewnick et al., 2015). The latter mainly depends on \( T_{\nu} \), interaction between particle and vapourizer surface, vapourizer design and molecular speeds. In the SV for \( T_{\nu} > T_{\nu, t} \) (Fig. 13), the peak width of three species followed the order of \( \text{NH}_4\text{NO}_3 < \text{NaNO}_3 < (\text{NH}_4)_2\text{SO}_4 \), all within 0.5 ms. Compared to the SV, PToF distributions in the CV showed broader peak widths, indicating longer vapour desorption/escape times. The peak width ratios between the CV and SV, defined as broadening ratios, vary widely between species: \( \sim 5.5 \) for \( (\text{NH}_4)_2\text{SO}_4 \), 2 for \( \text{NH}_4\text{NO}_3 \) and 1.8 for \( \text{NaNO}_3 \). The broadened peaks in the CV, leading to lower particle size resolution, degrade size distribution measurements in laboratory studies with monodisperse particles. For example, a small doubly charged peak of \( \text{NaNO}_3 \) observed with the SV cannot be separated in the CV (Fig. 13b1–2).

However, size distributions in ambient air tend to be broad, and when the size calibration curve of \( (\text{NH}_4)_2\text{SO}_4 \) is applied, a consistent size distribution measurement between the SV and CV is found, suggesting that the size distribution measurement in the CV is still useful (Hu et al., 2017).
Comparison of total detected signal in PToF vs. MS mode

As discussed above, the MS and PToF modes integrate detection timescales of milliseconds and seconds respectively. Thus the total signal ratio between PToF and MS modes can be used as an alternative tool for studying the vapourization rates of different species, as shown in Fig. 14.

For NH$_4$NO$_3$, PToF/MS of both vapourizers at low $T_v$ (200–400 °C) showed a continuously increasing trend, consistent with faster vapourization and decomposition/desorption as $T_v$ increased (Fig. 15a). PToF/MS ~ 1 for NO$^+$ and NO$_2^+$ was observed in both vapourizers for $T_v$ = 450–700 °C. For $T_v$ > 650 °C, the PToF/MS of NO$^+$ and NO$_2^+$ continuously decreased in the CV, suggesting a less efficient quantification from PToF than MS mode, in agreement with the broadened PToF peaks (Fig. 13a3) at those $T_v$. PToF/MS for NaNO$_3$ increased continuously until reaching 1 at 500 and 550 °C for the CV and SV respectively (Fig. 15b), which is consistent with the PToF widths vs. $T_v$ (Fig. 13b1-3). For sulfate (Fig. 15c), the PToF/MS ratio in both vapourizers increased with $T_v$ between 300 and 800 °C. This increase was mainly associated with faster vapourization/detection.
Based on all the $T_v$-dependent experiments discussed above, we recommend an operating $T_v \sim 500–550^\circ C$ for the CV for normal usage. In this temperature range, fast vapourization of inorganic particles with high CE and reduced distortion of PToF distributions are observed, while fragmentation (including of organic species) is less increased, and slower response effects observed at high $T_v$ (e.g. $>700^\circ C$) can be avoided.

4 Conclusions

To reduce the quantification uncertainty of non-refractory aerosols due to particle bounce in the AMS, a CV has been designed with the goal of trapping particles inside the vapourizer body to achieve near unity collection efficiency, thereby reducing one of the largest uncertainties associated with the AMS quantification which is particle bounce.

The performance of the CV was quantified and compared with the SV for four inorganic standard species NH$_4$NO$_3$, NaNO$_2$, (NH$_4$)$_2$SO$_4$ and NH$_4$Cl, representative of ambient nitrate, sulfate, ammonium and chloride species. The whole range of practical $T_v$ (200–800$^\circ C$) was explored. The main conclusions are as follows.

Thermal decomposition is a key step in aerosol detection in the AMS. The fragmentation patterns of inorganic species in the CV shift toward smaller mass fragments compared with the SV. This shift is caused by a greater degree of thermal decomposition in the vapourizer due to the increased residence time of condensed and/or vapour phase molecules on the walls of the CV.

Multiple results support the unlikelihood that a dominant fraction of NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$ and NH$_4$Cl vapourize as intact molecular species, but rather that they first decompose to NH$_3$(g) + acids (and other anion product species).

The CE of NH$_4$NO$_3$, NaNO$_3$, (NH$_4$)$_2$SO$_4$ and NH$_4$Cl in the CV at 500–600$^\circ C$ were $\sim 1$, $\sim 0.95$, $\sim 0.8$ and $\sim 0.35$ respectively, which are comparable to or higher than those in the SV ($\sim 1$, $\sim 0.85$, $\sim 0.4$, and $\sim 0.25$), indicating a reduced fraction of particle loss due to bouncing in the CV. Although the CE of some pure inorganic species were still less than 1 in the CV, a higher CE ($\sim 1$) has been observed for ambient internally mixed particles (Hu et al., 2017).

In this study, we found a temperature-dependent trend of the mass ratio between CO$_2^+$ produced and NO$_3$ sampled in the SV (1–10 %) likely due to catalytic reactions liberating charred carbon on the vapourizer. In the CV, negligible CO$_2^+$ ($< 0.4$ %) was formed when sampling NH$_4$NO$_3$ particles. NaNO$_3$ particle in the CV can produce a comparable amount of CO$_2^+$ per NO$_3$ mass to the SV (up to 10 %) when the CV has been recently exposed to high level of OA. Note that these CO$_2^+$/NO$_3$ ratios can be highly dependent on each individual instrument and its recent sampling history. In ambient air with typically negligible or very small submicron NaNO$_3$ concentrations, this CO$_2^+$ artefact should be much smaller for the CV than for the SV, and thus have a much lower interference for OA concentration and properties. It could also improve organic CO$_2$ quantification in source studies where ammonium nitrate $\gg$ OA (such as chamber studies with vehicle exhaust, Pieber et al., 2016).

The PToF distributions of species measured using the CV are broadened, which will reduce the size resolution. This effect will be most important for laboratory experiments with monodisperse particles. For ambient air with typically broad size distributions, size distributions measured from an AMS using the CV are expected to be useful (Hu et al., 2017). A method for estimating whether a pure species can be detected by the AMS sizing mode at a given $T_v$ is proposed.

Particle-beam position-dependent results showed that particle detection with the CV resembles the detection using the SV for NH$_4$NO$_3$, when the particle beam is focused on the edge of the CV. Minimal distortion in the PToF measurement can be achieved under this condition. For practical usage, this set up may be useful to increase size resolution in laboratory studies with monodisperse particles. Whether this benefit extends to less-volatile species should be investigated in future studies.
Based on all the results of $v$-dependent experiments, a $v \sim 500–550 ^\circ \text{C}$ for the CV is recommended.

**Data availability.** Data can be obtained from the authors upon request (jose.jimenez@colorado.edu)

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**Competing interests.** The authors declare that they have no conflict of interest.

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Supplement of

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

W. Hu et al.

Correspondence to: Jose L. Jimenez (jose.jimenez@colorado.edu)

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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$_{NH_4}$ are difficult to reconcile with this simple model (Jimenez et al., 2016). To explain this discrepancy, it has been proposed that NH$_4$NO$_3$ and (NH$_4$)$_2$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.

S1.1. Quantitative analysis of RIE$_{NH_4}$ when a fraction of NH$_4$NO$_3$ vaporizes as an intact salt

It has been suggested that the high RIE$_{NH_4}$ observed in the AMS can be explained by the vaporization of intact NH$_4$NO$_3$ 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$_{NH_4}$ of 4 based on this hypothesis with reasonable assumptions. This is even more so when considering values of RIE$_{NH_4}$ ~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$_{NH_4}$ 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$_4$NO$_3$(g) estimated by Chien et al. (2010) is actually realized at the AMS vaporizer temperature of approximately 600°C, which is much larger than the 64-92°C used in those experiments:
   a. NH$_4$NO$_3$ $\rightarrow$ 78% NH$_3$(g) + 78% H$_3$NO$_3^+$ (g) + 22% NH$_4$NO$_3$(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. $\frac{1}{2}$ of the H$_3$NO$_3$(g) is NO$_2$(g) and the other $\frac{1}{2}$ is HNO$_3$(g).

e. The molar fragmentation fraction for molecular NH$_4$NO$_3^+$ favors NH$_3^+$ more than proportionally to its mass fraction in the parent ion, as suggested by Murphy (2017). E.g.:
\[ \text{NH}_4\text{NO}_3^+ \rightarrow 50\% \text{NH}_3^+ + 50\% \text{HNO}_3(g) + 50\% \text{NH}_3(g) + 50\% \text{HNO}_3^+ \]

With those assumptions \( \text{RIE}_{\text{NH}_4} \sim 1.1 \). If one assumes in (d) 100\% of either NO\(_2\)(g) or HNO\(_3\)(g) for H\(_2\)NO\(_3\)^+(g), then \( \text{RIE}_{\text{NH}_4} \sim 1.05\text{-}1.12 \) can be obtained. If one assumes in (e) that the fragmentation of \( \text{NH}_4\text{NO}_3^+ \) yields 75\% \( \text{NH}_3^+ \), \( \text{RIE}_{\text{NH}_4} = 1.5 \) (if one assumes 100\% \( \text{NH}_3^+ \), then \( \text{RIE}_{\text{NH}_4} = 2.1 \)). Thus even with aggressive assumptions, the hypothesis is not consistent with the observed \( \text{RIE}_{\text{NH}_4} \) values of 4\text{-}14. It is very likely that the \( \text{NH}_4\text{NO}_3(g) \) fraction under (a) is much lower in the AMS (due to the 520\(^{\circ}\text{C} \) higher \( T_v \)), probably near zero. If we assume a value of 5\%, and the rest of the default assumptions above, then \( \text{RIE}_{\text{NH}_4} \sim 0.7 \). Thus it seems very difficult to quantitatively explain the observed \( \text{RIE}_{\text{NH}_4} \) with the Murphy (2017) hypothesis with reasonable assumptions.

For reference, Figure S4 shows the estimated \( \text{RIE}_{\text{NH}_4} \) estimated in this way as a function of the two key parameters. To obtain values of \( \text{RIE}_{\text{NH}_4} = 4 \) and larger, one needs to assume that a very large fraction of \( \text{NH}_4\text{NO}_3 \) vaporizes as \( \text{NH}_4\text{NO}_3(g) \) (far higher than the upper limit reported at 80\(^{\circ}\text{C} \)), AND that the fragmentation of \( \text{NH}_4\text{NO}_3^+ \) very strongly favors \( \text{NH}_3^+ \) ions. Importantly, the high vaporized fraction of \( \text{NH}_4\text{NO}_3(g) \) would also need to be achieved for mixed ambient particles with high organic and low \( \text{NH}_4\text{NO}_3 \) fractions, in order for this hypothesis to be consistent with ambient observations.

S1.2. Other evidence against the vaporization of a major fraction of \( \text{NH}_4\text{NO}_3 \) 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 \( \text{NH}_3(g) \) and the anions in the detection process (Fig. 4 in the main text).

(b) The constancy of the fragmentation pattern of \( \text{NH}_3(g) \) 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\textsubscript{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\textsubscript{4}\textsuperscript{+} 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\textsubscript{3}\textsuperscript{+} 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\textsubscript{4}\textsuperscript{+} ions formed from ammonium were detected more efficiently than the NO\textsubscript{x}\textsuperscript{+} (and SO\textsubscript{x}\textsuperscript{+}) ions, that effect could contribute to a larger-than-expected RIE\textsubscript{NH\textsubscript{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 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$_4$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 NH$_4^+$ 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$_4$NO$_3$. 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$_{\text{NH}_4}$ 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 RIE$_{\text{NH}_4}$ 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.
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$_4$NO$_3$; (b) 250 nm (NH$_4$)$_2$SO$_4$; (c) 300 nm NaNO$_3$; (d) 300 nm NH$_4$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).
Figure S4 Estimated RIE$_{NH4}$ as a function of the assumed fraction of NH$_4$NO$_3$ vaporizing as NH$_4$NO$_3$(g), and the fraction of NH$_x^+$ ions formed from the fragmentation of NH$_4$NO$_3^+$. Also marked is the upper limit fraction of NH$_4$NO$_3$(g) evaporated at ~80°C (Chien et al., 2010)
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)
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$_{\text{NH}_4}$ and the NO$_2^+$/NO$_\text{+}$ ratio as a function of HR-AMS vaporizer bias voltage while sampling pure NH$_4$NO$_3$ particles. Only ~2% variation is observed for RIE$_{\text{NH}_4}$ across the optimum tuning region, while ~8% variation is observed for the NO$_2^+$/NO$_\text{+}$ ratio.
References:


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.


