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To cite this article: D. M. Murphy (2016) The effects of molecular weight and thermal decomposition on the sensitivity of a thermal desorption aerosol mass spectrometer, Aerosol Science and Technology, 50:2, 118-125, DOI: [10.1080/02786826.2015.1136403](https://doi.org/10.1080/02786826.2015.1136403)

To link to this article: <https://doi.org/10.1080/02786826.2015.1136403>



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Accepted author version posted online: 31 Dec 2015.
Published online: 21 Jan 2016.



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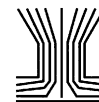
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The effects of molecular weight and thermal decomposition on the sensitivity of a thermal desorption aerosol mass spectrometer

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ABSTRACT

In free molecular flow the slower speed of heavier molecules means that they spend more time in the ion source of a mass spectrometer. Hence the sensitivity of the thermal desorption mass spectrometers such as the Aerodyne Aerosol Mass Spectrometer (AMS) should include a term that scales as the square root of the molecular weight. Thermal decomposition on the vaporizer reduces the molecular weight prior to ionization and changes electron impact cross-sections. Thermal decomposition therefore has the potential to change the sensitivity, in some cases by more than a factor of three. Current AMS calibrations that rely upon an ammonium nitrate calibration and scaling for other components with a relative ionization efficiency may overestimate the concentration of large, thermally stable molecules and underestimate small or thermally unstable molecules. The overall sensitivity of the AMS to organics includes a partial cancellation of these effects. There is an incomplete understanding of the vaporization process, including that of ammonium nitrate.

ARTICLE HISTORY

Received 13 July 2015

Accepted 11 December 2015

EDITOR

Paul J. Ziemann

Introduction

The AMS is a widely used instrument for analysis of the chemical composition of aerosol particles (Jayne et al. 2000). It has successfully measured the concentration of sulfates, nitrates, and organics in atmospheric aerosols (Canagaratna et al. 2007), as well as providing important information about the oxidation state of the organics. While it is feasible to calibrate for a few of the most abundant molecules such as ammonium sulfate, it is not feasible to calibrate for every one of the many thousands of organic compounds in organic aerosols. Instead, the calibration for ammonium nitrate is transferred to organic species using approximate electron impact ionization cross-section (Canagaratna et al. 2007). This existing calibration method for the AMS for organics relies on the hypothesis that the sensitivity expressed as ion current per unit mass is approximately independent of the molecular weight (Jimenez et al. 2003; Canagaratna et al. 2007; Canagaratna et al. 2015). Here it is shown that this sensitivity is significantly affected by free molecular flow in the ion source and thermal decomposition on the vaporizer.

Number density in free molecular flow

The rate I at which ions are formed is given by

$$I = C n \sigma, \quad [1]$$

where C is the efficiency of the ion source including the intensity of the electron beam and other factors, n is the number density in the ion source, and σ is the electron impact ionization cross-section. The cross-section of most small molecules is approximately proportional to the number of electrons which, in turn, is approximately proportional to the molecular weight (Jimenez et al. 2003). The assertion was then made that since the number of ions is the product of the number of molecules and the cross-section, the number of ions is approximately proportional to the mass of each class of species in the aerosol (Jimenez et al. 2003; Canagaratna et al. 2007).

However, this contains an implicit assumption that n , the gas phase concentration in the ion source, is proportional only to constant factors and N , the number of molecules that evaporate. This is not true in free molecular flow.

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As a simple case, consider a Knudsen cell closed on one end, a small hole at the other end, and a constant mass flux of evaporating material at the closed end. The mass flux leaving the hole is $A M n \bar{c}/4$, where A is the area of the hole, M is the mass of each molecule, and \bar{c} is the mean molecular velocity. Mass balance shows that the steady state concentration is

$$n = \frac{\dot{m}}{A} \sqrt{\frac{2\pi}{kTM}} \quad [2]$$

where \dot{m} is the evaporating mass flux.

If there is an electron beam inside this tube and the ionization cross-section is proportional to M , then the ion current at a given mass flux is proportional to the square root of the molecular weight as well as the total mass flux.

The AMS ion source is in the free molecular flow regime. The ion source chamber pressure is reported as about 2×10^{-5} Pa (Drewnick et al. 2005) so the mean free path is large compared to the ion source dimensions. The presence of the beam of air molecules from the inlet means the pressure is somewhat higher in the ion source itself than it is in the ion source chamber. However, vacuum pumping calculations for the air load indicate the pressure in the ionization region must still be in free molecular flow. It would take exceptionally high aerosol loadings for evaporating aerosols to add significantly to the gas load from the air beam. Another simple argument for free molecular flow in the ion source is that it would not work properly in continuum flow: the electron beam would be disrupted and any ions formed would suffer collisions with gas molecules.

A rapidly particle evaporating on the vaporizer may produce a transient region of continuum flow around the evaporation point. This region is small compared to the distance from the vaporizer to the electron beam. If evaporated instantaneously, a 500 nm diameter particle contains enough molecules to produce a mean free path of very roughly 50 μm in a 50- μm diameter hemisphere of gas, with the exact value depending on the composition. As the gas expands, the density decreases with the cube of the expansion so that the mean free path is many centimeters by the time the gas molecules have moved less than a millimeter.

Free molecular flow will prevail all the way to the surface of slowly evaporating particle. The time scale between “quickly” and “slowly” evaporating may be roughly estimated as the time for a typical gas molecule to travel a mean free path away from the particle. The mean time for 500°C molecules with a molecular weight of 80 to travel 50 μm is less than 200 ns. As an example, a particle that takes several microseconds to evaporate would have the evaporating gas molecules traveling away

faster than they could accumulate above the surface. Since the characteristic time for molecules to move one mean free path from the surface is similar to the time constant for heat transfer within a particle (see details below), it would take detailed modeling to determine if it is possible to have even a small region of continuum flow near the particle.

The AMS ion source is not at steady state. Instead, there are pulses of gas as individual aerosol particles volatilize. A simple simulation with pulsed evaporation is shown in Figures 1 and 2. 300,000 molecules with masses of 50 or 200 atomic units evaporate during a 4 μs time period. Over the entire 400 μs period of the simulation, the mean numbers of molecules in the box representing an electron beam are 1091 and 2170, respectively. As predicted for steady state from Equation (2), the mean number densities are in a ratio of 1:2, the square root of the ratio of molecular weights.

Although the results are not sensitive to the assumed evaporation time, there is a rationale to the choice of 4 μs . The evaporation time for ammonium nitrate particles must be much faster than the observed ~ 25 μs pulses of ions from single particles (Jayne et al. 2000; Drewnick et al. 2015). It seems unlikely that particles will evaporate faster than the time it takes for heat transfer from the side of the particle to the center. This time scale varies as b^2/α , where b is a characteristic dimension and α is the thermal diffusivity (Bird et al. 1960, ch. 11.1). For a 500-nm diameter particle with a thermal diffusivity similar to water this characteristic time is roughly 450 ns. This 4 μs is chosen here simply as a (logarithmic) middle ground between these time scales. Figure S1 shows the effect of assuming a constant evaporation rate over 100 μs .

Figure 2b shows the peak shape for ions formed from vaporized ammonium nitrate at a 420°C vaporizer temperature (Jayne et al. 2000). The points are offset in time since in the original figure $t = 0$ was at the peak ion current rather than the start of evaporation. The simple molecular flow model reproduces the fast rise and slower fall of the ion current as well as the approximate width of the peak, which for ammonium nitrate should be between the widths for molecular weights of 50 and 200. The match in shape and approximate length supports the use of a free molecular flow model. The exact length and especially the tail of the evaporation pulse will be due to the exact dimensions of the ion source as well as molecules getting trapped in pores or temporarily adsorbing elsewhere on either the vaporizer or surfaces in the ion source (Drewnick et al. 2015). Complete dimensions of the AMS ion source are not published but the electron beam is as close as feasible to a 3.8-mm diameter vaporizer (Drewnick et al. 2005).

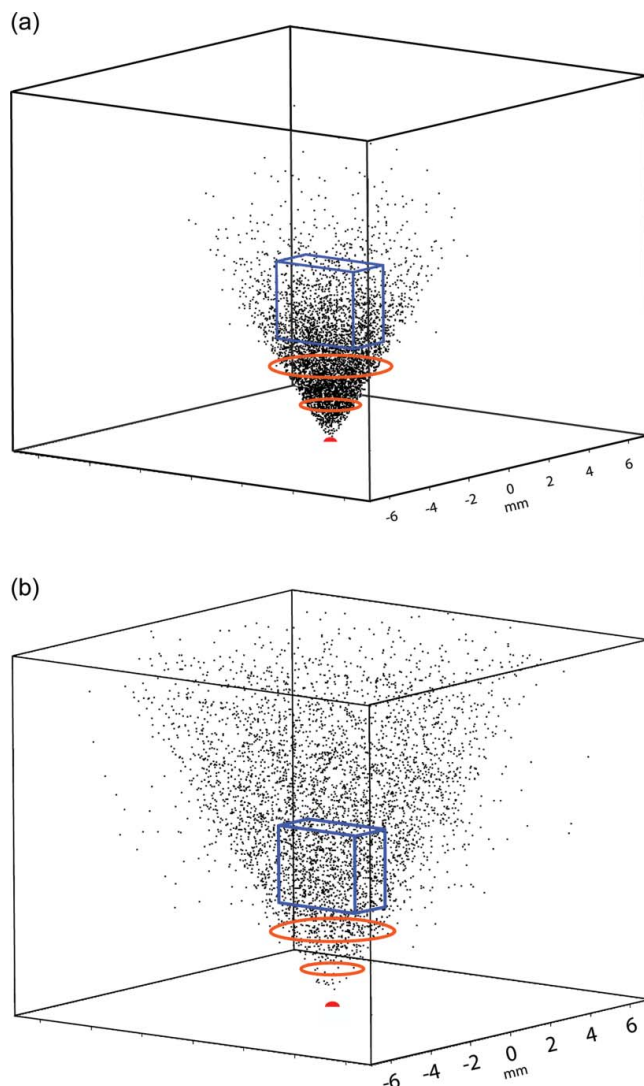


Figure 1. The positions of 5000 (of 300,000 simulated) molecules with molecular weight 50 evaporating over a $4\ \mu\text{s}$ interval at $10\ \mu\text{s}$ (upper) or $20\ \mu\text{s}$ (lower) after the onset of evaporation. Molecules originate from a point source at the large (red) dot near the bottom of a 3 mm deep cone with 3 mm inner diameter. This simple model has no collisions between molecules and no ion source plates. Molecules are counted if they are inside a $1.5 \times 3 \times 3\ \text{mm}$ box starting 1 mm above the top of the conical vaporizer. The molecules are tracked after leaving the initial point and every collision with the cone with Lambertian distributions in direction and Maxwell-Boltzmann velocity distributions with a translational temperature of 773 K.

Figures 1 and 2 are calculated for a particle evaporating near the bottom of the cone. The molecular weight dependence is the same for other geometries. For example, a calculation with a particle evaporating from a point $2/3$ of the way up the side of the cone resulted in the same molecular weight dependence, just with fewer molecules in the electron beam. Modeling the vaporizer as a flat surface instead of a cone also changes the absolute number of molecules in the electron beam but not the dependence on molecular weight.

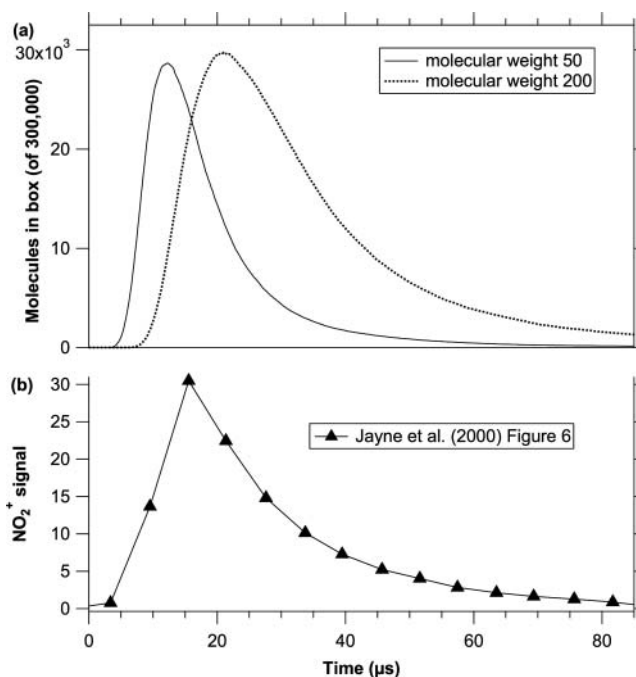


Figure 2. (a) The number of molecules in a $1.5 \times 3 \times 3\ \text{mm}$ electron beam starting 1 mm above the top of a 3 mm deep cone. (b) The time dependence of ions from single ammonium nitrate particles in the AMS (Jayne et al. 2000).

All cases (analytical steady state, $4\ \mu\text{s}$ evaporation, different electron beam or vaporizer dimensions, and a slower evaporation case in Figure S1 in the online SI) show a square root relationship for the mean number of molecules in the electron beam as a function of molecular weight. Further collisions of neutral molecules with other surfaces in the ion source may change the overall probability of passage through the electron beam but not the molecular weight dependence. Molecular weight changes the speed of the molecules in free molecular flow but not their spatial distribution. This is a general feature of free molecular flow into a well-pumped chamber (Behrens 1987).

A square root dependence of sensitivity on molecular weight was used by Dzepina et al. (2007) for AMS analysis of polycyclic aromatic hydrocarbons but has not been followed up on, with later papers continuing to use a sensitivity independent of molecular weight (Canagaratna et al. 2015).

Figure 3 shows the relative sensitivity per unit mass of an AMS or similar instrument after accounting for the residence time in the ion source. The electron impact ionization cross-sections (circa 70 eV) are mostly from Harrison et al. (1966). Some very light organics in Harrison et al. that are not relevant to aerosols are not plotted; even the larger molecules available are generally smaller or less oxygenated than those relevant to ambient aerosol particles. Cross-sections for H_2O and NH_3 are from Lampe et al. (1957). Tetraethoxysilane (TEOS) is shown

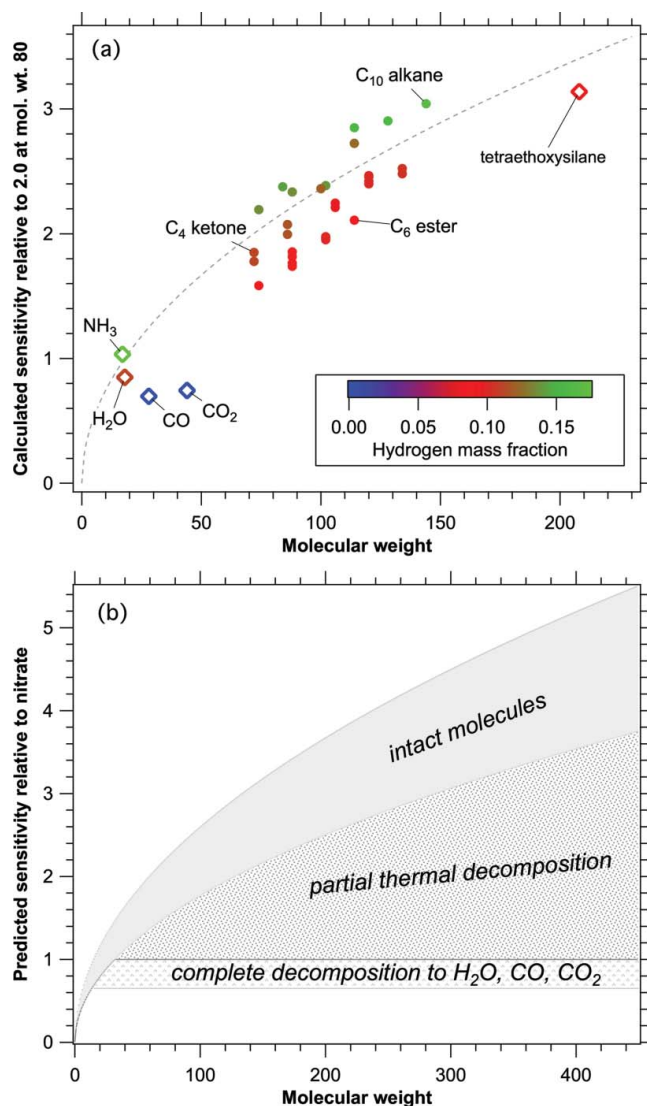


Figure 3. (a) The estimated relative sensitivity per unit mass of an electron impact ion source to various intact molecules with a residence time varying as the square root of the mass (dashed curve). Departures above and below the dashed curve are due to the ionization cross-sections being larger or smaller than typical value per unit mass. (b) The expected range of sensitivity depending on the amount of thermal decomposition on the vaporizer.

as one of the few large molecules with a measured cross-section (McConkey et al. 2008). The vertical scale is relative but is normalized to two at a molecular weight of 80 because the sensitivity of the AMS is usually referenced to the nitrate ions from ammonium nitrate and a factor of about two is appropriate if roughly half of the ions from ammonium nitrate are NO₂⁺ or other nitrate fragments (Canagaratna et al. 2007).

Thermal decomposition

The residence time in the ion source is reduced if high molecular weight organics decompose on the vaporizer

into smaller neutral molecules with a speed appropriate to their mass rather than the slower parent molecule. Without thermal decomposition, the residence time factor could become very large, as secondary organic aerosol includes molecules with molecular weights exceeding 600 (Baltensperger et al. 2005).

Because of extensive fragmentation during electron impact ionization, the mass of the observed ions offers only a lower limit on the mass of the neutral molecules. Ion fragments are smaller at higher vaporizer temperatures (Alfarra 2004). This could be caused either by thermal decomposition during vaporization or by increased fragmentation during electron impact ionization of intact molecules with more vibrational energy.

Softer ionization methods such as vacuum ultraviolet ionization (VUV) can give more information about the volatilized molecules, although hot molecules can fragment even very close to the VUV threshold (Nir et al. 1999). Canagaratna et al. (2015) observed extensive decomposition of oxygen-rich organic compounds into H₂O, CO, and CO₂ volatilized at temperatures as low as 200°C. In contrast, several investigators have observed parent or similar (e.g., MH₂O) ions from large organic molecules volatilized at up to 300 or 400°C (Sykes et al. 2002; Wilson et al. 2006; Shu et al. 2013). However, the latter studies did not generally use VUV photons with enough energy to directly ionize gas-phase H₂O, CO, or CO₂, so there is probably no contradiction.

The aerosol heating rate in the AMS brings particles from near room temperature to near 600°C in somewhere between a fraction of a microsecond and tens of microseconds. This rate is close to thermal desorption by lasers with microsecond rather than nanosecond pulses. Cation attachment to intact organic molecules with molecular weights over 400 has been observed for CO₂ laser desorption with pulse lengths of 0.15 or 10 μs (Posthumus et al. 1978; Hahn et al. 1987). Large molecules can also desorb intact from shorter pulses (Öktem et al. 2004). As with the VUV ionization, this only shows that some molecules survive intact, not that decomposition does not occur.

Data on thermal decomposition of bulk samples are unlikely to be informative because of the competition between the kinetics of evaporation and decomposition (Posthumus et al. 1978). The evaporation time of the ammonium nitrate particles shown in Jayne et al. (2000) is orders of magnitude faster than even fast bulk heating techniques such as Curie-point foils (Neusüss et al. 2000). Thermal decomposition can also take place either during evaporation or during collisions of gas molecules with the vaporizer walls. For the approximate geometry in Figure 1 almost 90% of the molecules that go through the electron beam have at least one wall collision subsequent to evaporation near the bottom tip of the cone.

Discussion

Thermal decomposition introduces several new issues. Due to the combination of molecular weight and ionization cross-sections, the AMS may be about one third to one fourth as sensitive per unit mass of H_2O , CO , and CO_2 fragments compared to intact organic molecules with molecular weights of 100–150 (Figure 3). Second, thermal decomposition opens the possibility of a type of charring whereby some less volatile material would be left behind after decomposition. If this evaporates sufficiently slowly it would not be counted as aerosol mass. Third, thermal decomposition creates the possibility of matrix effects. The presence of water or other solvents can change the competition between evaporation of intact molecules and thermal decomposition. Matrix assisted laser desorption and ionization (MALDI) instruments depend on such effects to volatilize intact macromolecules. No significant matrix effects were observed in the AMS for sulfate in ammonium sulfate particles coated with water or dioctyl sebacate or for mixtures of sulfate and nitrate (Hogrefe et al. 2004; Matthew et al. 2008). Matrix effects may be more likely with large organic molecules that undergo extensive thermal decomposition. Shu et al. (2013) observed that the thermal decomposition of mixtures of organic compounds was different than that for the pure substances.

Two examples demonstrate the potential importance of thermal decomposition. About 50% of the ion current from citric acid particles is due to H_2O^+ , CO^+ , and CO_2^+ (Canagaratna et al. 2015). If these ions are mostly due to neutral H_2O , CO , and CO_2 formed on the vaporizer, then because of the low sensitivity to these molecules (Figure 3), they must represent an even larger percentage of the mass. One self-consistent solution is that about 75% of the mass is neutral H_2O , CO , and CO_2 with the balance neutrals with an average molecular weight of about 100. Simple algebra from Figure 3 shows that the overall sensitivity would be about one third that of intact citric acid.

AMS instruments are calibrated using the NO^+ and NO_2^+ ions from ammonium nitrate (Canagaratna et al. 2007). Based on an almost identical sensitivity to ammonium in either sulfate or nitrate, it has been assumed that ammonium nitrate vaporizes to ammonia and nitric acid (Allan et al. 2004). However, the electron impact cross-section of ammonia is less than half that of nitric acid (Jimenez et al. 2003) and the residence time ratio from the square root of the molecular weights is another factor of almost 2. Therefore, if ammonium nitrate thermally decomposed to ammonia and nitric acid, there would be about four times as many NO^+ and NO_2^+ ions

as NH^+ , NH_2^+ , and NH_3^+ ions. Instead, there are slightly more ammonium fragment ions (Jayne et al. 2000; Ng et al. 2011). This is not consistent with electron impact ionization of gas phase ammonia. The vaporization pulse lengths of the ammonium fragments are also very similar to that of the NO_2^+ ion (Drewnick et al. 2015), supporting the concept that they come from the same neutral molecule. Whether or not that is intact ammonium nitrate or another vaporization product, these calculations show that the sensitivity to ammonium can change by more than a factor of 4 depending on how ammonium nitrate thermally decomposes on the vaporizer.

Since AMS sensitivities are referenced to nitrate, whether or not ammonium nitrate thermally decomposes affects the interpretation of other calibrations. The idea that ammonium nitrate probably evaporates to species other than gas phase ammonia and nitric acid may be counterintuitive to those used to working with ammonium nitrate aerosols under typical atmospheric conditions. But in the AMS the evaporation is many orders of magnitude faster, occurs at a much higher temperature, and the neutral molecules travel into a vacuum rather than diffusing into air. The evaporation could be studied using tunable VUV ionization. For example, urea particles impacting a similar vaporizer do not produce gas-phase ammonia (Fang et al. 2011).

One reviewer suggested that since ammonia and water are light molecules with high sensitivity in the AMS they provide counterexamples to the concepts presented here. However, even if there is no dependence of ion source residence time on molecular weight, the electron ionization cross-section of NH_3 is just not large enough to explain the measured AMS sensitivity to ammonium. So the neutral evaporating species from ammonium cannot be ammonia gas unless there is some novel mechanism not included either here or in standard AMS analyses. Although the sensitivity to ammonium in nitrate and sulfate is nearly identical (Hogrefe et al. 2004), there is a much lower sensitivity to ammonium in ammonium oxalate (Takegawa et al. 2007). The tungsten vaporizer surface could complicate the situation because both NH_3 and HNO_3 can be converted to NO on $\sim 400^\circ\text{C}$ tungsten oxide surfaces with the NH_3 response especially variable depending on surface history (Roberts et al. 1988). Whatever the vaporization process, ambient ammonium measurements of ammonium nitrate and sulfate are still correct because they are based on calibrations.

For water, the evidence is mixed. Aerosol water can be difficult to measure in the AMS because of background from gas-phase water and because of evaporation in the focusing inlet followed by both condensation and evaporation during and after the expansion into vacuum.

Measured vacuum aerodynamic diameters can sometimes be influenced more by changes in aerosol shape with drying than by mass loss (Zelenyuk et al. 2006; Matthew et al. 2008). Overall, there is no clear consensus on the relative sensitivity for water (Matthew et al. 2008; Engelhart et al. 2011; Mensah et al. 2011).

According to Equation (2), the number density and hence sensitivity depends on temperature as well as molecular weight. Limited data suggest that a Maxwell-Boltzmann velocity distribution at close to the filament temperature is appropriate for aerosol impacting on a filament (Sykes et al. 2002). The effect on sensitivity of molecules volatilizing with different translational temperatures would be fairly small because the range of absolute temperature is small compared to the possible range in mass.

The molecular weight and thermal decomposition effects described here apply to all versions of the AMS with a vaporizer and an ion source in free molecular flow, including high-resolution versions and the chemical speciation monitor. A few other thermal desorption mass spectrometers have been constructed besides the Aerodyne AMS. One used for measurements of organic vapor pressures did not account for residence time in the ion source (Chattopadhyay et al. 2001). The effect on the inferred vapor pressures is very small because each experiment uses only one molecule over a small range in absolute temperature. A thermal desorption mass spectrometer used to measure stratospheric aerosols containing nitric acid relied on direct calibration (Schreiner et al. 2002), avoiding issues with residence time. Sykes et al. (2002) correctly described how faster neutral molecules result in lower sensitivity at higher temperatures.

The sensitivity of the AMS to organics needs to be evaluated in light of the dependence on molecular weight. It is likely that thermal decomposition is partially compensating for the high molecular weight of many organics in aerosol particles. An overall change in sensitivity to organics in ambient particles by as much as a factor of two is unlikely because of reasonable self-consistency using the current sensitivity. Because the sensitivity to organics depends on their composition, changes in calibration may be small in some situations and larger in others. There may be more subtle effects than an overall scale factor. For example, differences in molecular weight and thermal decomposition could cause a difference in sensitivity to primary and secondary organics. There may have been some laboratory kinetics experiments in which an apparent increase or decrease in AMS mass could be better explained as a change in molecular weight or thermal decomposition. Although the discussion here emphasizes organic molecules, the variation in

sensitivity with residence time in the ion source also applies to inorganic species.

There are few data available to directly evaluate the importance of molecular weight to sensitivity. There are no papers describing a systematic calibration of the AMS for organic aerosols. There are data for seven organic species in a PhD thesis (Alfarra 2004). They show over a factor of 10 range in absolute sensitivity and factors of 2 to 3 decreases in sensitivity when the vaporizer temperature was increased from 500 to 750°C. Neither behavior is easy to explain quantitatively, although there is a general increasing trend in sensitivity with molecular weight and the temperature dependence could be due to increased thermal decomposition above 500°C as well as particles bouncing off of the vaporizer without evaporating.

It may be possible to estimate and partially compensate for the residence time effect with information in the mass spectra. First, a significant fraction of the peak at m/z 44 is due to CO_2 from thermal decomposition (Canagaratna et al. 2015). As a marker for the amount of thermal decomposition it may have a correlation with sensitivity as well as oxygen content.

Second, the vaporization length for a given m/z peak is determined by a combination of evaporation time, adsorption, and the molecular weight of the vaporized molecules responsible for that peak. For quickly evaporating particles, there can be information on the molecular weight of species. For example, from Figure 2 one can infer that the molecule responsible for the NO_2^+ peak has a molecular weight considerably less than 200. Studies along the lines of Drewnick et al. (2015) for many more peaks and aerosol types may put limits on thermal decomposition. It should be possible to put bounds on the molecular weight of the neutral molecules in the ion source with the ion fragments providing a lower limit and the vaporization length providing an upper limit. It is not clear how close these bounds will be.

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